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HAZARDOUS WASTE TREATMENT TECHNOLOGY

Chemical & Biological Detoxification Branch
Alternative Technologies Division
Hazardous Waste Engineering Research Laboratory
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Hazardous waste may be stored, treated and disposed in a variety of ways. Treatment technology exists today for detoxification or destruction of wastes in an environmentally-acceptable manner through physical, chemical and biological means. This volume covers several common alternative technologies for treatment of hazardous wastes as well as several emerging alternative technologies that show promise for future application. Thermal destruction of wastes through incineration, reaction with molten glass, etc., is not included as part of this effort.

Alternative technologies are taken to be those that provide treatment techniques for waste other than landfilling, landfarming, or lagooning. These alternatives are further subdivided into existing and emerging technologies depending on whether or not they have been proven in full scale tests and adopted for commercial use.

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small business in handling their wastes responsibly and economically.

This report describes a variety of chemical and biological treatment alternatives applicable to hazardous wastes as well as several emerging treatment alternatives for physical, chemical or biological separation/detoxification of hazardous wastes. Alternative technologies are generally those that provide for waste handling techniques other than landfilling or land application. This report further restricts its coverage of alternatives to exclude physical separation and those techniques that are characterized as thermal processes. In the emerging alternative treatment area, considering those technologies that show promise but are not past experimental or testing stages, this report presents physical, chemical and biological treatment techniques but not thermal processes.

For further information, please contact the Alternative Technologies Division of the Hazardous Waste Engineering Research Laboratory.

David G. Stephan, Director
Hazardous Waste Engineering Research Laboratory

ABSTRACT

Hazardous waste may be stored, treated and disposed in a variety of ways. Treatment technology exists today for detoxification or destruction of wastes in an environmentally acceptable manner through physical, chemical and biological means. This volume covers several common alternative technologies for treatment of hazardous wastes as well as several emerging alternative technologies that show promise for future application. Thermal destruction of wastes through incineration, reaction with molten glass, etc., is not included as part of this effort.

Alternative technologies are taken to be those that provide treatment techniques for waste other than landfilling, landfarming, or lagooning. These alternatives are further subdivided into existing and emerging technologies depending on whether or not they have been proven in full scale tests and adopted for commercial use.

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SECTION I

INTRODUCTION

Physical, chemical and biological treatment comprise a set of technology tools that can be used to prevent the release of hazardous materials into the environment or alter their nature so that they are no longer an environmental problem. For example, chemical methods can be used to recover metals, such as chromium, from waste streams. Not only does chemical treatment remove toxic metals from streams being discharged into the environment, natural and often scarce resources may be conserved and recycled as well. We are not limited, however, to chemical methods in this example of metals removal. Bacteria and other organisms manufacture metal-binding proteins and other substances that are capable of removing metals with a high degree of specificity. Furthermore, whereas chemical methods are most useful for removing the bulk of metals from waste streams, biological processes are better at removing low but still toxic concentrations of metals. Thus, chemical and biological methods complement each other here as they frequently do in other treatment situations as well.

Physical treatment methods can be used as separate techniques or as adjuncts to chemical or biological methods. Ultraviolet light, for example, destroys dioxins. Micro-wave heating, on the other hand, provides a practical way to increase the temperature of contaminated soils and thus enhance either biological or chemical destruction of PCBs or dioxins. Additionally, physical separation techniques may be utilized to concentrate large volumes of dilute wastes for more efficient application of detoxification technologies. Reverse osmosis, pressure filtration, sedimentation, etc. are proven methods for removing contaminents for further treatment, storage or disposal. Emerging techniques such as the use of reversible gel materials for removal of water

from contaminated aqueous streams, may develop as generally accepted treatment technologies of the future.

Chemicals have the ability to alter the nature of materials and this fact accounts for the rather wide applicability that chemical treatment has in the area of hazardous waste destruction. It is possible, for example, to take the now-banned pesticide, ethylene dibromide (EDB), and convert it chemically to the salt, potassium bromide (which has economic value), and the gas, acetylene. Other chemical approaches modify hazardous materials so that they become non-toxic. Glycol-based chemical reagents, for example, remove a chlorine atom from 2,3,7,8-dioxin converting the dioxin to a non-toxic adduct. Here again, chemical and biological methods complement each other for, once a single chlorine atom is removed from the dioxin molecule, the partially-dechlorinated dioxin is much less toxic to microorganisms and is consequently subject to natural biological decomposition to harmless salts and gases.

Biological organisms produce specialized chemicals, i.e., enzymes, that also have an ability to alter the nature of pollutants. With modern advances in genetic engineering, biotechnology will assume greater importance in this field as time goes by. Currently available technologies such as activated sludge treatment or rotating biological contactors may also be used in limited applications for hazardous waste treatment. Research is progressing, however, to identify naturally occurring organisms such as the white rot fungus, Phanerochaete chrysosporium, that can degrade chlorinated organics, and to produce genetically altered organisms that may be developed in the laboratory with genes to specifically code for enzymatic systems capable of detoxifying hazardous wastes.

Physical, chemical and biological treatment technologies can be applied to pollution control and abatement in industrial waste streams, soils, sediments and natural ground waters and surface waters. It is important, therefore, for the purpose of setting regulations that prevent, control or clean up the discharge of hazardous wastes to the environment that the technologist seek out and evaluate applicable existing technologies, and to develop new and emerging technologies when other avenues for pollution control are not available.

SECTION II

ALTERNATIVE CHEMICAL AND BIOLOGICAL TREATMENT TECHNOLOGIES

A. CHEMICAL TREATMENT

1. Neutralization

Process Description --

Neutralization involves combining either an acid or a base with a hazardous waste stream to adjust liquid pH to acceptable levels. Neutralization may be required prior to waste treatment to protect downstream equipment and optimize treatment performance. The pH of an acid or base should not be confused with its acidity or basicity, which is the volume of base or acid required to reach a specified pH. The final desired pH is usually between 6.0 and 9.0, and the reaction products include water, salts, and solids precipitated by pH dependent solubility reactions.

Equalization is usually provided before waste neutralization to control fluctuations in flow and strength. Neutralization is most commonly performed in completely mixed corrosion resistant tanks, although ponds and limestone filter beds are also used. Lime, calcium hydroxide, caustic soda, soda ash and ammonium hydroxide are common bases; sulfuric acid, hydrochloric acid and nitric acid are common acids used for neutralization. Absorption towers and aerated tanks utilize carbon dioxide in air to form carbonic acid in water.

Neutralization may be conducted in batch or continuous flow modes and is frequently conducted in a series of tanks. The process is usually controlled automatically using feed back, feed forward or multimode controllers. Solids removal is usually required either after neutralization or in a separate clarifier to remove precipitated solids. Figure 1 shows a typical neutralization system.

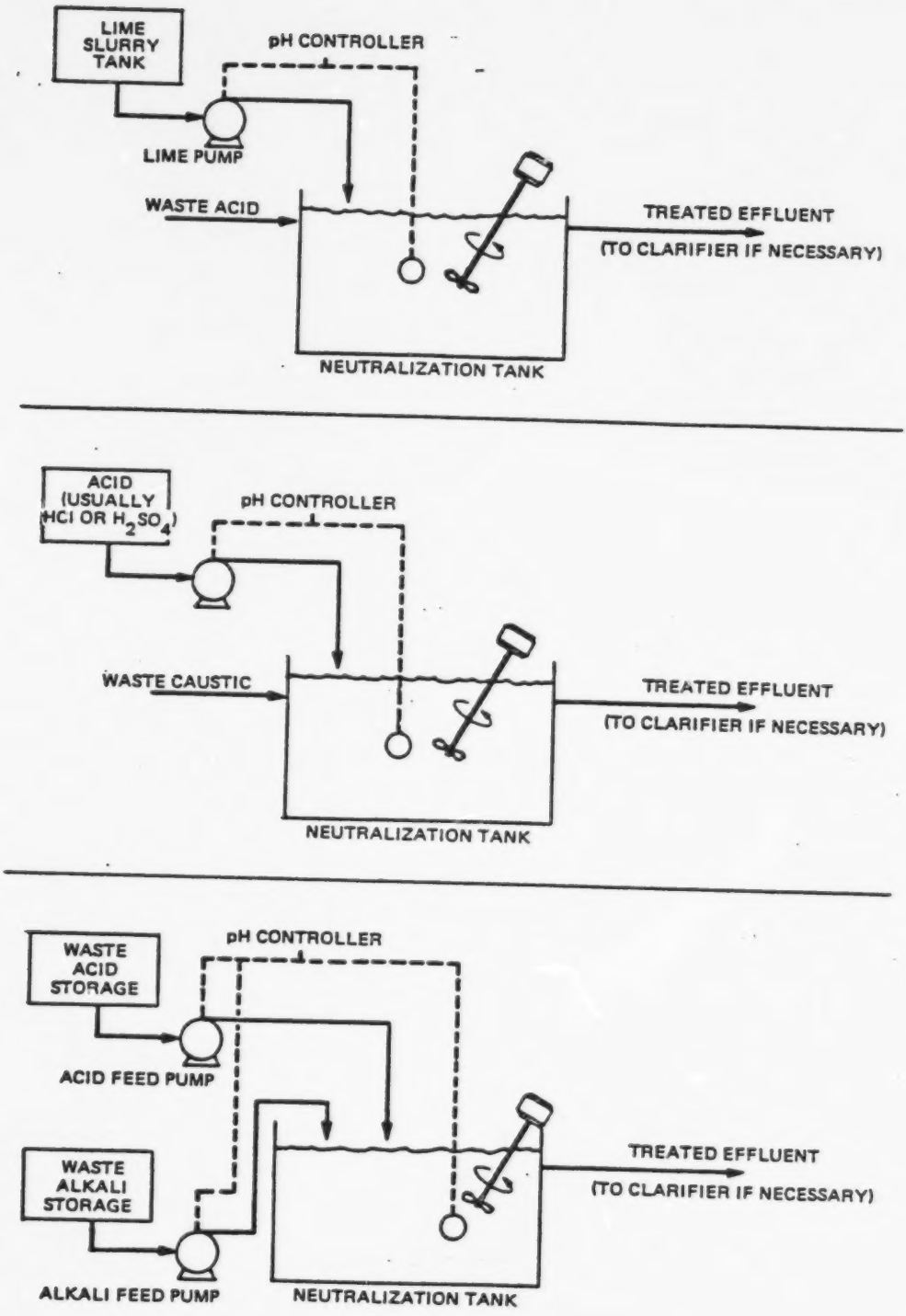


FIGURE 1. NEUTRALIZATION

Applicability to the Treatment of Hazardous Waste --

Neutralization is employed at almost all commercial hazardous waste treatment facilities. Depending upon the types of treatment processes operated at each facility, neutralization may occur at different points in the treatment process. For example, of seven facilities visited, four treated metal-laden aqueous wastes by precipitation at high pH. Therefore, neutralization of these waste streams did not occur until the metals removal step had been accomplished.

The neutralization process at hazardous waste facilities was also carried out with chemicals arising from different sources. Since most commercial hazardous waste facilities treating corrosives accept wastes of both low and high pH, judicious pretreatment of these wastes allow them to be used to effect the final pH adjustment as well as the initial pH adjustments required for other treatment processes. The concept of "waste to treat waste" was practiced at one commercial hazardous waste treatment facility where spent caustic waste from tin refining was being used to neutralize acidic metal plating wastes.

While relatively straightforward in theory, neutralization continues to be one of the most common and critical processes used in the hazardous waste treatment industry.

Environmental Considerations --

Caution should be exercised when mixing strong wastes to insure that the byproducts of neutralization are not hazardous. Extreme heat and toxic gases, including ammonia, hydrogen sulfide and hydrogen cyanide, may be liberated if wastes are not mixed slowly and are not properly pretreated. Additional treatment will usually be required after neutralizing hazardous wastes to remove dissolved and suspended metals and organics. Neutralization, or pH adjustment, is a key step in removing heavy metals (see Chemical Precipitation). Solids

precipitated during neutralization are more readily removed by sedimentation and filtration after flocculation.

The high dissolved solids concentration in neutralized wastes may produce chemical complexes which are not effectively removed by sedimentation and filteration. Additional treatment by chemical addition, carbon adsorption, ion exchange or reverse osmosis may be required to treat complexed wastes.

2. Chemical Precipitation

Process Description --

Chemical precipitation is a physico-chemical process in which a dissolved contaminant is transformed into an insoluble solid, facilitating its subsequent removal from the liquid phase by sedimentation or filtration. The process usually involves 1) adjustment of pH in order to shift the chemical equilibrium to a point that no longer favors solubility, 2) addition of the chemical precipitant, and 3) flocculation in which precipitate particles agglomerate into larger particles.

Equipment requirements include a reaction tank and agitator, chemical storage tanks and chemical feed pumps. Precipitation may be done on a batch or continuous basis. Figure 2 presents a typical flow schematic for a chemical precipitation system.

Applicability to the Treatment of Hazardous Waste --

The most common existing application of precipitation for treatment of hazardous waste is the removal of toxic heavy metals from aqueous hazardous waste. This includes the removal of arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc.

Usually, metals are precipitated from solution as hydroxides, sulfides, or carbonates. Hydroxide precipitation with lime or caustic soda is most common.

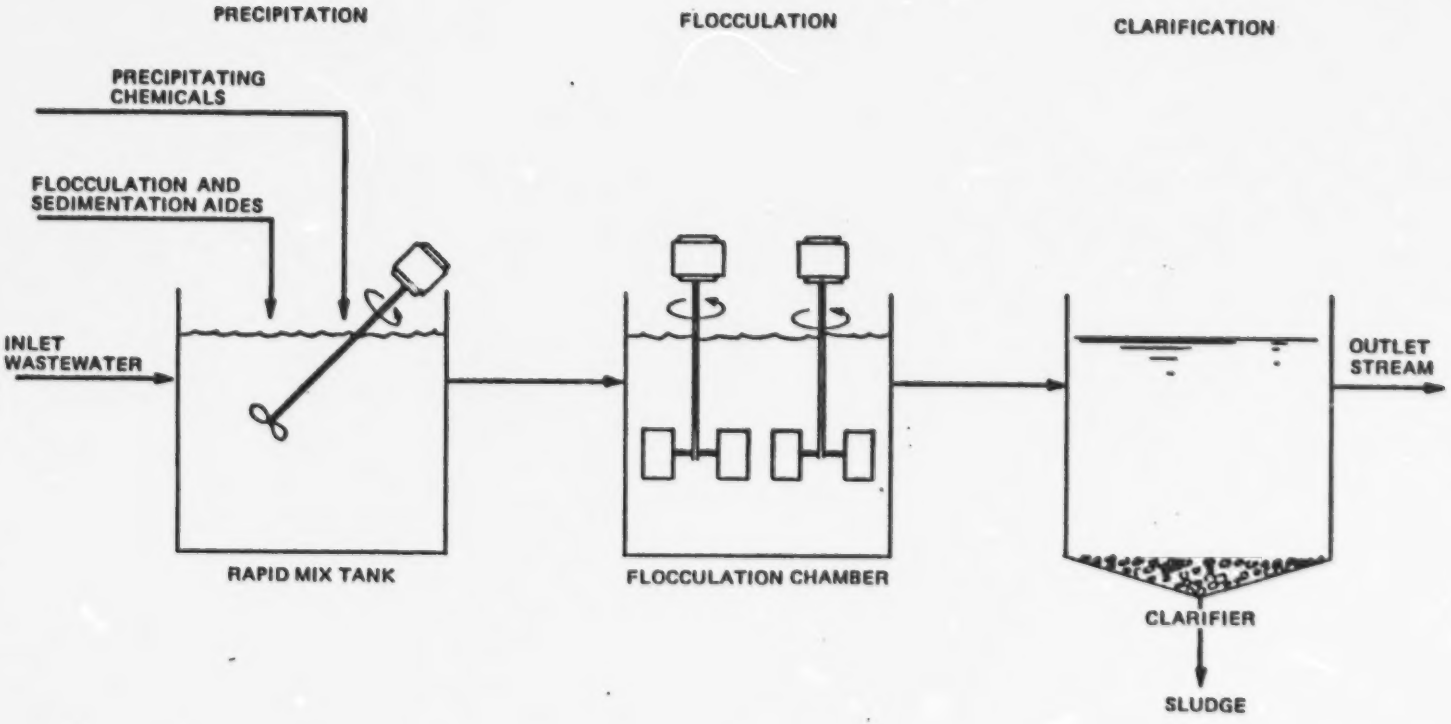


FIGURE 2. CHEMICAL PRECIPITATION AND ASSOCIATED PROCESS STEPS

Because the optimum pH for hydroxide precipitation is different for each metal ion, treatment of mixed-metal aqueous wastes requires compromise. Generally, hydroxide precipitation is carried out at a pH between 9.5 and 12. Effluent heavy metal concentrations less than 1 mg/l are theoretically achievable, but the presence of complexing agents like ammonia, cyanide, and EDTA may keep higher concentrations of metals in solution.

Metal sulfides are generally much less soluble than hydroxides thus better removal efficiencies are achievable. Sulfide can also be used to precipitate metals in the presence of complexing agents and over a broader pH range than possible for hydroxide precipitation.

Other potential applications include the removal of precipitable substances from certain nonaqueous liquids, such as waste organic solvents. For precipitation, flocculation and sedimentation to be effective, the viscosity of the liquid must not be overly high. While it may be possible to induce certain precipitation reactions within highly viscous wastes such as liquid organic polymeric wastes, flocculation and sedimentation would be greatly inhibited.

Specific applications in which precipitation is used for the treatment of liquid wastes containing hazardous substances are numerous. Several representative examples include the following:

- A naval shipyard in New England uses a combination of hydroxide, carbonate and sulfide precipitation for the removal of heavy metals from their steam generator cleaning and metal finishing wastes. Because this waste also contains ammonia and the chelating agent EDTA, two pretreatment steps - aeration or steam stripping at alkaline pH to remove ammonia and precipitation of EDTA as the free acid at low pH - are required prior to metals precipitation.

° A commercial facility which treats metal-laden aqueous hazardous waste uses two-stage precipitation, dosing with a caustic to pH 11, followed by pH adjustment with alum to 9.5 and then dosing with sodium bisulfide. The influent wastewater may contain up to 300 ppm Cd, 15,000 ppm Cr, 10,000 ppm Cu, 120,000 ppm Fe, 10,000 ppm Pb, and 10,000 ppm Ni. Wastes accepted for treatment at this facility do not contain any chelating agents. After flocculation with anionic and cationic polyelectrolytes and clarification in a solids-contact clarifier, the aqueous effluent meets permit requirements for discharge to the municipal sewer. The sludge, thickened, dewatered and solidified with lime, has gone to a landfill.

° At a small hazardous waste treatment/recycling facility, custom small-batch treatment of single-metal aqueous wastes produces high metal content sludges from which the metal value can be reclaimed. Specifically, an aqueous waste containing 125 mg/l copper is precipitated with sodium carbonate, and centrifuged to produce a copper carbonate sludge with greater than ten percent by weight copper.

Environmental Considerations --

The precipitation process, followed by one or more solid/liquid separation steps, produces an aqueous effluent which may require further treatment and a heavy metal sludge. Sludge is typically dewatered to greater than 20 percent solids. Various chemical fixation and stabilization processes may be applicable to the dewatered sludge. When sulfide is used to precipitate metals, excess sulfide in the aqueous effluent may create environmental problems including the risk of hydrogen sulfide generation if the effluent is mixed with a low pH aqueous stream.

3. Chemical Oxidation

Process Description --

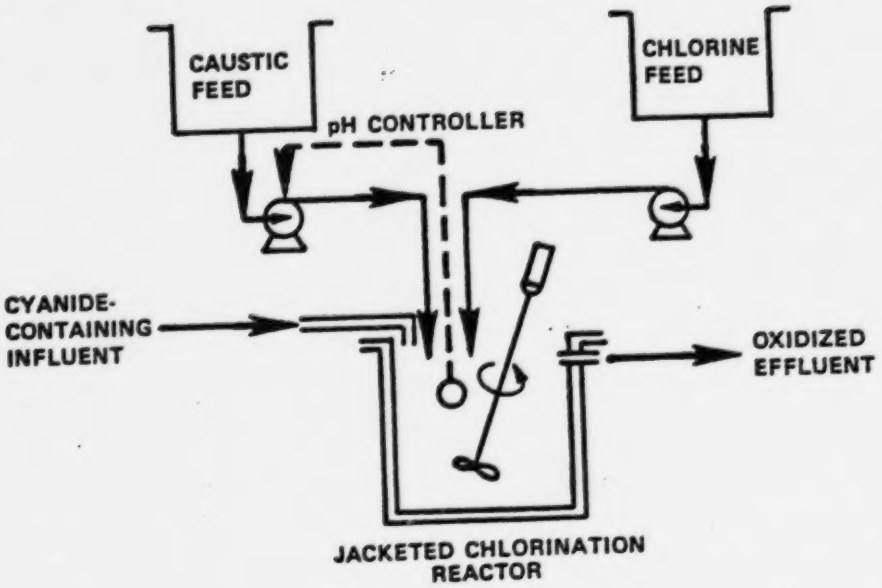
Chemical oxidation is a process which oxidizes ions or compounds to render them non-hazardous or to make them more amenable to subsequent removal or destruction processes. Species are oxidized by the addition of a chemical oxidizing agent which is itself reduced.

Chemical oxidation requires simple reaction equipment. Storage tanks are required for oxidizers, pH adjustment materials (e.g., lime) as needed, and feed stock. Reactors are typically enclosed cylindrical tanks with rapid-mix agitators. Monitoring and control of pH may be needed, and an oxidation-reduction potential (ORP) electrode probe is useful to measure reaction progress. Oxidation can occur as a batch or continuous reaction. A sample chemical oxidation scheme for cyanide destruction by alkaline chlorination is shown in Figure 3 and ozonation is shown in Figure 4.

Applicability to the Treatment of Hazardous Waste --

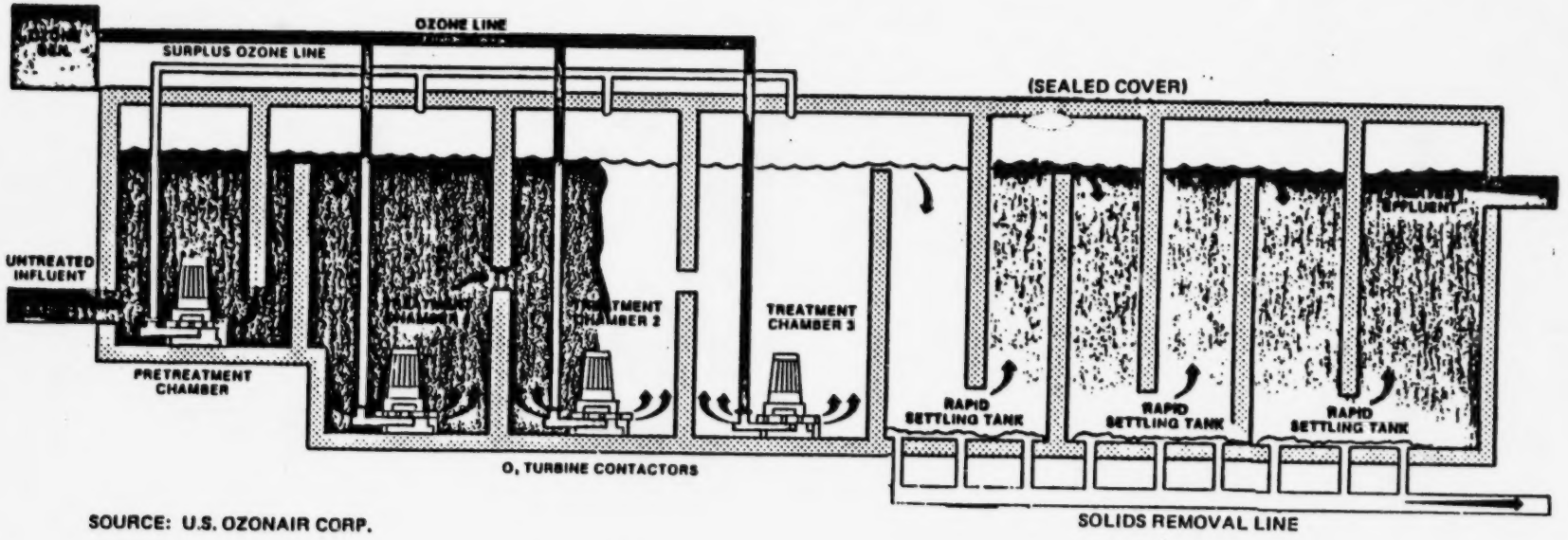
Chemical oxidation has been used to treat hazardous organic and inorganic contaminants in aqueous solution. Its major use has been for treating cyanide in plating wastes. In this process, chlorine gas, chlorine dioxide, or hypochlorite (sodium or calcium) are routinely used to destroy cyanide (CN^-), which is converted to nitrogen gas (N_2) and carbon dioxide gas (CO_2). Other less common oxidants include potassium permanganate ($KMnO_4$), hydrogen peroxide and ozone.

Potassium permanganate has been experimentally used for destruction of trace organics (including aldehydes, mercaptans, phenols, and organic acids) in aqueous hazardous waste and drinking water. It has also recently been used to treat non-chlorinated pesticides.



SOURCE: LANCY INTERNATIONAL, ZELIENOPLE, PA

FIGURE 3. SAMPLE CHEMICAL OXIDATION (ALKALINE CHLORINATION OF CYANIDE)



SOURCE: U.S. OZONAIR CORP.

FIGURE 4. TREATMENT OF LIQUIDS CONTAINING HAZARDOUS WASTES BY OZONATION

Cyanide destruction by chlorine oxidation is common among metal plating and finishing operations which use cyanide. Calgon, Lancey, Dupont, and Oxy-metal Industries, among others, offer pre-engineered systems, of which the alkaline chlorination (hypochlorite plus caustic) process is typical.

Chemical oxidation is most useful for dilute aqueous wastes. Chemical oxidants are relatively non-selective and may oxidize other compounds present in the waste prior to oxidizing the contaminant of concern, e.g., the cyanide or metal. As a result this process has limited application for slurries, tars and sludges which may contain large amount of oxidizable components.

Certain transitional metal ions, e.g. soluble iron, interfere with alkaline chlorination of cyanides, though in general, mixed cyanide and heavy metal solutions are treated successfully if sufficient reaction time (24 hours) is allowed. Adjustment and control of the waste pH is also critical for the cyanide destruction process. $KMnO_4$ is expensive and not as widely used for cyanide destruction, although it requires no pH maintenance as with chlorine destruction to prevent generation of hydrogen cyanide gas. Hydrogen peroxide has been employed to a certain degree but requires a catalyst and decomposes in dilute aqueous solution and high metal concentration (Kiang and Metry, 1982).

Cyanide destruction by chemical oxidation can be carried essentially to completion within 2-24 hours, depending upon the extent of interfering conditions. Potassium permanganate removal of trace organic compounds (<1 ppm) appears to be good, and hydrogen peroxide destruction of selected metals provides similar efficiencies (Kiang and Metry, 1982).

At one commercial hazardous waste treatment facility, aqueous cyanide wastes are treated in a batch alkaline chlorination process. The batch size is 5000 gallons. The hypochlorite used as an oxidant is a waste stream from a chloralkali manufacturing facility, containing 8-9 percent free chlorine. Caustic is used to keep the pH elevated, generally between 8.5 and 10.0. The average reaction time for cyanide degradation is two hours. This facility accepts cyanide containing sludges and solids as well as liquids. Typically, these are heat treating salts with up to 5 percent cyanide. Solids are mechanically fragmented and then dissolved in hot water with 5 percent caustic prior to mixing with aqueous cyanide wastes for alkaline chlorination.

At another facility, hydrogen peroxide is used to reduce the COD of certain aqueous wastes in a batch pretreatment tank. The treated effluent is then mixed with other metal-laden wastes for further treatment by chemical precipitation.

Ozonation is another chemical oxidation process appropriate for aqueous streams which contain less than 1.0 percent oxidizable compounds. Ozone can be used to pretreat wastes to break down refractory organics before biological or other treatment. Biorefractory compounds in toluene diisocyanate, ethylene glycol, and ethylene dichloride contaminated aqueous process wastes are oxidized to a biodegradable form by ozone. Ozonation is found to improve the biotreatability of water containing styrene by transforming it to a compound such as benzoic acid. It can also be used as a polishing step after biological or other treatment processes to oxide untreated organics. Industries currently use ozone for on-site treatment of hazardous wastes to destroy cyanide and phenolic compounds. The rapid oxidation of cyanides with ozone offers advantages over the slower alkaline chlorination method. The metal finishing and

petrochemical industries utilize ozone for treatment of aqueous hazardous wastes and it is also applicable to aqueous coke making wastes in iron and steel manufacturing. Ozone must be produced on site.

A combination of UV radiation and ozone has been demonstrated to economically treat certain halogenated organics including aldrin, chlorinated phenols, dieldrin, endrin, ethylene dichloride, kepone, methylene chloride, PCB, DDT and pentachlorophenol. Aldehydes, ketones, alcohols, aromatic hydrocarbons, ethers, carbonyl compounds, chlorinated aromatics (pesticides), nitroso compounds, and saturated hydrocarbon groupings are all oxidizable with ozone. Bis (2-ethylhexyl) phthalate, benzene, anthracene, benzo(a)pyrene, benzo(k)fluoranthene, pyrene, benzoic and perbenzoic acids, styrenes, and aqueous waste from petrochemical processes producing toluene diisocyanate, ethylene glycol, styrene monomers and ethylene dichloride have also been successfully pretreated by ozonation before biological treatment.

Environmental Considerations --

In general, the residuals from chemical oxidation processes that must be managed properly include the liquid effluent, off-gases, and any precipitates produced.

The alkaline chlorination process may produce metal hydroxide precipitates if certain metals are present in the incoming hazardous wastestream. In addition, dissolved organics which are not completely oxidized by the alkaline chlorination process may be transformed into chlorinated organics which would be carried off in liquid effluent. Finally, the chlorine and caustic residuals may have to be neutralized prior to discharge of the liquid effluent.

The ozonation process may not completely oxidize organic pollutants to carbon dioxide and water, and additional treatment is often required. Effluent

from ozonation reactors may require treatment to destroy ozone residuals. These residuals may damage piping and equipment or endanger worker health. Precautions must be taken with all ozone generation and reaction equipment to ensure worker safety.

Precipitation of oxidized metals (e.g., iron) will produce sludges which may require treatment and/or disposal. Partial oxidation of organics may produce toxic and/or odorous by-products. Overdosing of oxidant will produce an oxidant residual in the aqueous effluent which may adversely impact other downstream treatment processes.

4. Chemical Reduction

Process Description --

Chemical reduction involves the transfer of reactive electrons from one compound to another, and is used to either render compounds nontoxic, or to enable compounds to undergo chemical destruction or physical removal. Metals, in particular hexavalent chromium, are reduced through the addition of a compatible reducing agent, for example, reduced sulfur compounds. Specific solution pH and agitation requirements must be met to ensure successful chemical reduction. Figure 5 depicts chemical reduction of hexavalent chromium.

Applicability to the Treatment of Hazardous Waste --

Chemical reduction is best applied to liquid wastes free of organic compounds. It is widely used in industry to control hexavalent chromium waste, and to remove and/or recover mercury from mercury cells used in chloralkali manufacturing. Chromium is usually reduced by sodim sulfite salts, or sulfur dioxide. Iron, aluminum, and zinc have also been identified as potential chrome reducing agents. Caustic sodium borohydride ($NaBH_4$) has been commercially employed to reduce mercury to elemental form, allowing its recovery. $NaBH_4$

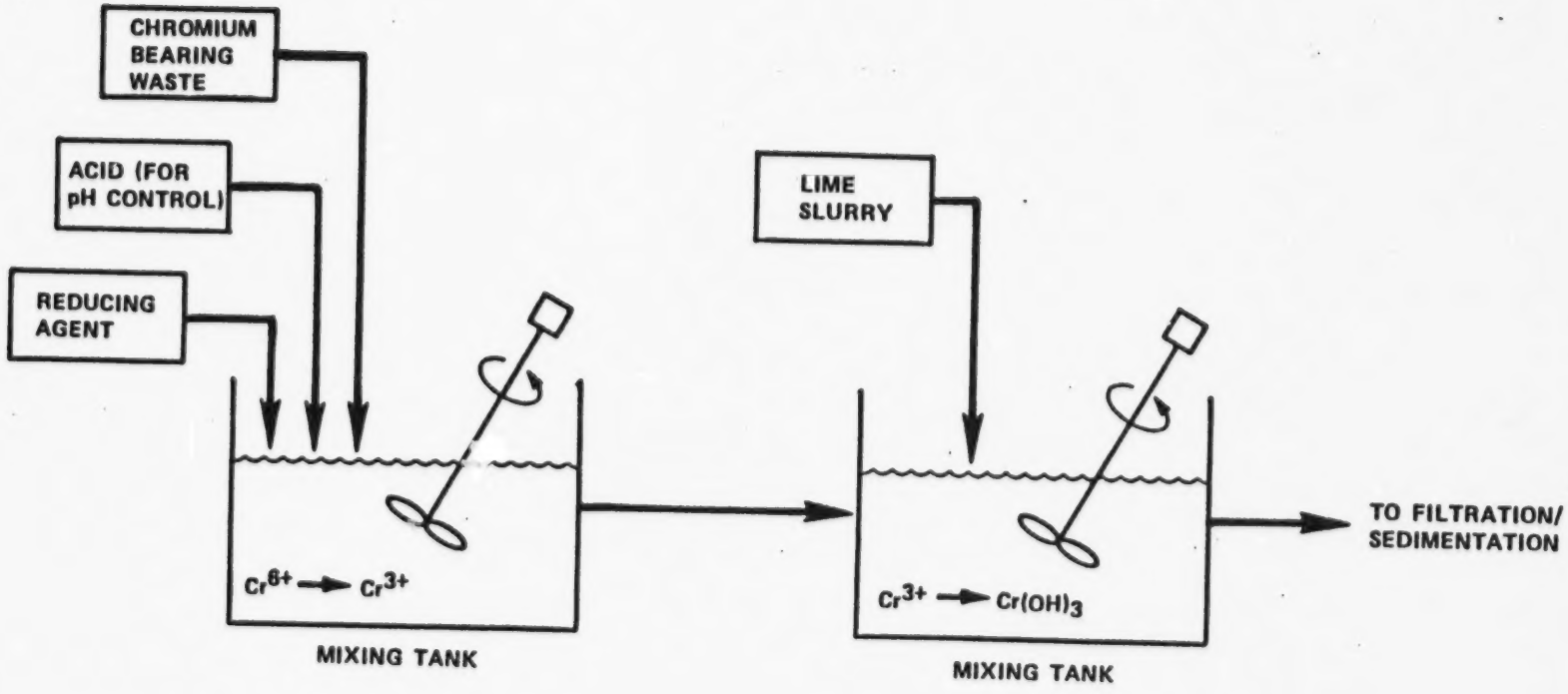


FIGURE 5. CHEMICAL REDUCTION OF HEXAVALENT CHROMIUM (Cr^{6+})

is also now used on a commercial scale to reduce soluble lead, including organo-lead salts from tetra-alkyl lead manufacturing aqueous wastes; and to reduce and recover silver from photographic operations.

Chemical reduction is also a common hazardous waste technology for reducing complexed or chelated metals, such as copper and nickel, found in aqueous metal plating waste. The solution pH is adjusted to break the metal-chelate bond, then the reducing agent is added to reduce the metal and precipitate it out of solution. Filtration often follows.

Chrome and mercury reduction facilities are numerous in the United States. Pre-engineered systems are available from a number of vendors. Lead and silver reduction and removal units are much less common though these processes appear to operate on a commercial scale for metal concentrations below 300 ppm (DeRenzo, 1978). Potentially banned hazardous wastes which are treatable with this technology include:

- hexavalent chromium
- relatively low concentrations of silver, nickel, copper, and other metals
- metal-containing cyanides
- soluble inorganic and organic lead
- inorganic mercury

Chemical reduction has limited application to treatment of slurries, tars, or sludge because surface contact is difficult to achieve between reducing agent and the hazardous constituent. Solid hazardous materials must be liquified prior to treatment by reduction. Because reducing agents are not selective, organic compounds present in treated solutions will decrease destruction efficiency and may liberate offensive odors. Mass reducing agents, sodium borohydride for example, are expensive. Mixing reducing agents and feed substrate

must be conducted carefully because violent reactions can occur if the reducing agent or feed material is added too quickly.

Efficiency of chrome and mercury reduction is high (>90 percent) and can occur within 1-2 hours in continuous processes. Longer reaction times will increase the destruction efficiency. Other metal reduction processes described above produce results which approach or match those efficiencies.

Environmental Considerations --

A major problem with chemical reduction of metals is the large volume of metal hydroxide sludges that can be generated. Even after dewatering, substantial waste quantities may need to be handled.

5. Chlorinolysis

Process Description --

In the chlorinolysis process, chlorine reacts with clorinated hydrocarbon wastes at temperatures of 500 to 800 deg. C and pressures of 1,000 psig or greater. The reaction products include carbon tetrachloride (CCl_4), perchloroethylene, trichloroethylene, anhydrous hydrogen chloride, unreacted hydrocarbons, and unreacted chlorine. The process steps include pretreatment of the wastes by filtration and/or distillation to remove water, solid materials, and incompatible compounds which are extraneous to the process; reaction with chlorine; distillation to separate the reaction products; and absorption of the hydrochloric acid solution that is produced.

Two versions of the chlorinolysis process have been developed. The Diamond Shamrock Corporation developed a process that utilizes high temperature and moderate pressure in a quartz-lined, nickel-lined carbon steel reaction vessel. The Hoechst Corporation of West Germany has developed a chlorolysis process that operates at lower temperature and higher pressure within a nickel-lined,

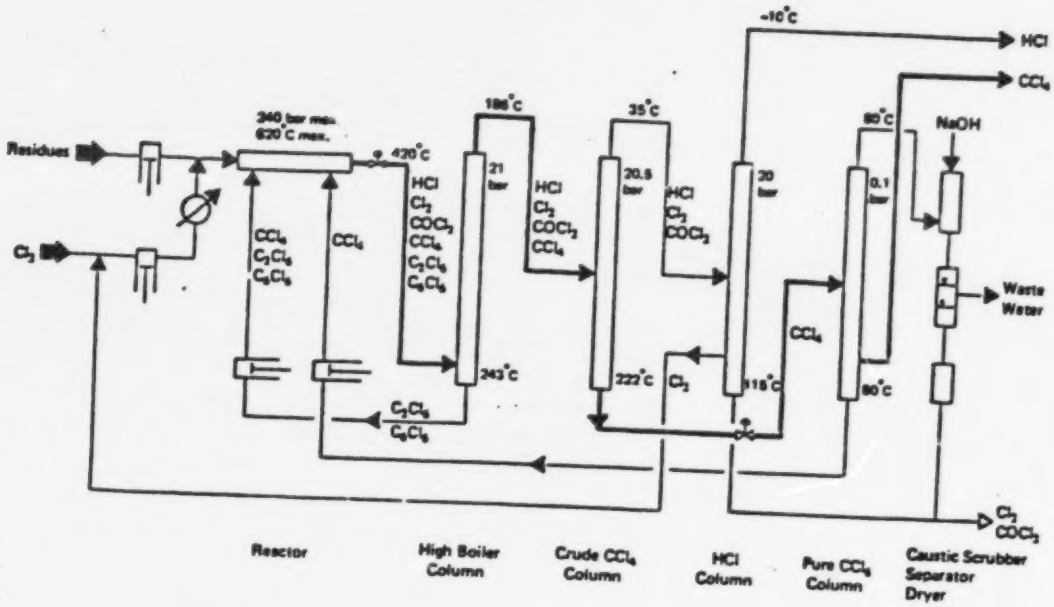
special stainless steel reactor. Figure 6 shows a process flow schematic for the Hoechst chlorolysis process.

Applicability to the Treatment of Hazardous Waste --

Chlorinolysis, developed as a production process for CCl_4 rather than a treatment process, is capable of producing salable CCl_4 from waste chlorinated hydrocarbons. Generally, the chlorinolysis process is suitable for conversion of chlorinated wastes and residues including, but not limited to, waste from the produciton of pesticides, vinyl chloride, herbicides and solvents. Thirteen pesticides which are amenable to chlorinolysis include aldrin, chlordane, DDD, DDT, ethylene dichloride, benzene hexachloride, heptachlor, lindane, o- and p-dichlorobenzene, pentac, perthane, and TCBB (GCA, 1984). Wastes to be used as a feed stock should contain only hydrogen, carbon and chlorine. The presence of other substances, such as sulfur, could result in corrosion; and phosphorus, nitrogen or oxygen could result in the production of unwanted by-products. In addition, feed streams must contain less than five percent aromatic compounds in order to limit the reaction temperature to the design temperature. Pretreatment is required to remove undesirable compounds. Chlorinolysis is operated on a large scale requiring an adequate continuous supply of chlorinated wastes to make the process feasible.

Environmental Considerations --

As previously stated, the presence of elements other than carbon, hydrogen, or chlorine in the feed will result in the production of unwanted by-products. In the case of the presence of oxygen or oxygenated compounds phosgene will be produced. Air emissions from the chlorinolysis process may include such pollutants as carbon tetrachloride, phosgene, hydrogen chloride, chlorine, and sulfur dioxide, resulting in the need for air pollution control equipment. Scrubber water from the process may be high in dissolved solids (GCA, 1984).



SOURCE: KREKELER H., H. SCHMITZ, D. REBHAN;
"THE HIGH PRESSURE CHLOROLYSIS OF HYDROCARBONS TO CARBON TETRACHLORIDE"

FIGURE 6. CHLORINOLYSIS PROCESS HOECHST AG

6. Wet Air Oxidation

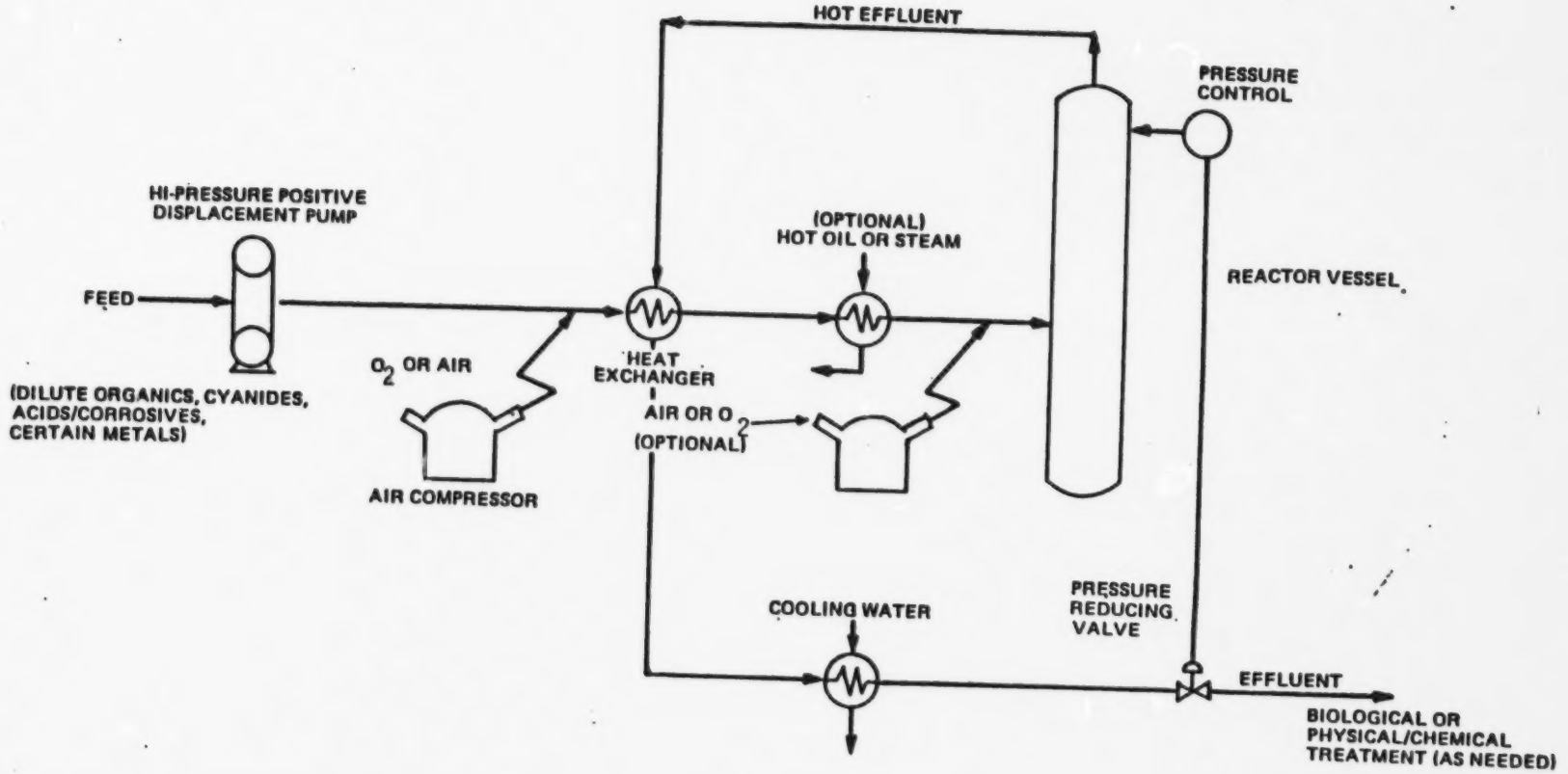
Process Description --

Wet air oxidation is the aqueous phase oxidation of dissolved or suspended organic or inorganic substances at elevated temperature (177 to 315 deg. C) and pressure (300 to 3000 psi). Elevated pressure is used to keep the water in its liquid state, allowing organic destruction to proceed at lower temperatures than would otherwise be necessary. Water serves to moderate the oxidation rate, removing excess heat of reaction (Kiang and Metry, 1982). Oxygen is incorporated as the oxidizing agent.

A typical schematic of process flow is presented in Figure 7. Feed materials are pressurized and pumped to a heat exchanger which pre-heats the feed and cools the reactor vessel effluent. Additional heat as needed is added to the pre-heated feedstock and/or the reactor vessel. Air or oxygen is injected prior to the heat exchanger or in the reactor. Reactor effluent not sufficiently cooled in the heat exchanger may require additional cooling. The effluent then travels through a pressure control valve to reduce its pressure to a normal atmospheric level.

After pressure let-down, the vapor and liquid components of the cooled effluent are separated. The vapor passes through an air pollution control system which may include a water scrubber and an activated carbon adsorption system or an off-gas incinerator. The aqueous effluent stream, which might contain low molecular weight organic acids, may be discharged to a subsequent treatment process for further treatment.

Wet air oxidation (WAO) converts hazardous wastes to less toxic substances. Reduced sulfur compounds, such as sulfides and mercaptans, are oxidized to inorganic sulfates; cyanides to carbon dioxide and ammonia or nitrogen gas;



SOURCE: CANNEY AND SCHAEFER, ZIMPRO, INC. 1984

FIGURE 7. WET AIR OXIDATION

chlorinated hydrocarbons to hydrochloric and simple organic acids; and metals to metal salts (Canney and Schaefer, 1983). Certain highly chlorinated aromatic organics such as pentachlorophenol, PCBs and DDT are resistant to destruction in the conventional WAO process. However, Zimpro reports that a proprietary cocatalyst system demonstrated at bench-scale enables greater than 99.5 percent destruction of these compounds by WAO at 275°F.

Applicability to the Treatment of Hazardous Waste --

Wet air oxidation can be used to oxidize any material, organic or inorganic, with an approximate COD value between 10,000 and 100,000 mg/l (California Department of Health Services, 1984). It is best suited to cyanide destruction and to pretreatmment of organics-containing aqueous hazardous wastes too toxic for biological treatment or too dilute for incineration (Canney and Schaefer, 1984).

This process is well-established for treatment of municipal sludges and industrial wastes, with over 180 installations in operation or under construction. Its commercial application to hazardous waste has been limited to date.

A commercial-scale wet air oxidation system has been developed by Zimpro, Inc., Rothschild, WI and at least four petrochemical companies in Japan have successfully treated acrylonitrile production aqueous wastes (Canney and Schaefer, 1984) by wet air oxidation. One commercial hazardous waste treatment facility uses a Zimpro skid-mounted WAO unit to process aqueous waste containing phenols, mercaptans, non-halogenated pesticides, solvents, and still bottoms (California Department of Health Services, 1984). This unit has a maximum operating capacity of 10 gpm with a one-hour reaction time. Stronger wastes are pumped through the unit at lower rates (as low as 0.5 gpm, but generally 3-4 gpm) to provide sufficient oxygen for reaction (air compressors are fixed

speed) and longer reaction times. Currently, only 3,000 to 50,000 gallons of aqueous hazardous waste are treated monthly by this WAO system. Operating temperature and pressure are about 500-550°F and 1600 psi respectively. The unit cannot handle suspended solids concentrations in excess of 1 percent. High inorganic concentrations in the waste streams treated, particularly metals in cyanide plating wastes, result in fouling of the heat exchangers. Therefore, the scale is periodically cleaned off by pumping five percent nitric acid through the system.

Environmental Considerations --

Wet air oxidation is not designed to be a stand-alone treatment process. It produces an aqueous effluent usually requiring further treatment and an off-gas. In addition, there may be a spent descaling acid stream in cases where wastes with high levels of metals or inorganic salts are treated.

The nature of the aqueous effluent and off-gas depends on the chemical characteristics of the influent waste. Complex organic compounds are generally converted to low molecular weight organic acids and other simple organics which may partition between the liquid effluent and the off-gas. Chlorinated organics result in production of hydrochloric acid which may make the aqueous effluent corrosive. Metal-containing wastes such as spent cyanide plating solutions produce a metal-laden effluent which would require treatment to remove the heavy metals. Cyanide itself produces ammonia; which may have to be scrubbed from the off-gas.

B. BIOLOGICAL TREATMENT

1. Activated Sludge

Process Description --

Activated sludge is a biological waste treatment process, so named because it involves the production of an active mass of microorganisms capable of stabilizing aerobically-biodegradable substances. The process operates by the continuous recycle of environment. The recycled biomass, in the presence of oxygen, decomposes the biodegradable organic matter by hydrolysis and oxidation. The end products of this operation are carbon dioxide, water and a waste residue.

There are numerous variations of the activated sludge process, however, fundamentally the principles of the unit operations are the same. Figure 8 illustrates a typical activated sludge system. The first step in the process involves aeration in an open tank, in which the organic biodegradable matter in the waste is degraded by microorganisms in the presence of oxygen. The hydraulic retention time of this unit operation is usually from 6 to 24 hours, although depending on the process mode, shorter or longer retention periods may be incorporated. This is followed by a sludge-liquid separation step in a clarifier. The clarified effluent is the treated product. A portion of the settled sludge is recycled back to the aeration basin to maintain the desired concentration of organisms. The excess is wasted and must be disposed.

Two variations of the conventional activated sludge process that have been used in treating aqueous industrial wastes are the UNOX process and the PACT system. The UNOX process (Union Carbide), or pure oxygen activated sludge process, uses pure oxygen instead of air to oxygenate the biomass. Pure oxygen systems support higher concentrations of microorganisms than conventional activated sludge systems and require a lower retention time. In the pure

ACTIVATED SLUDGE BIOLOGICAL TREATMENT

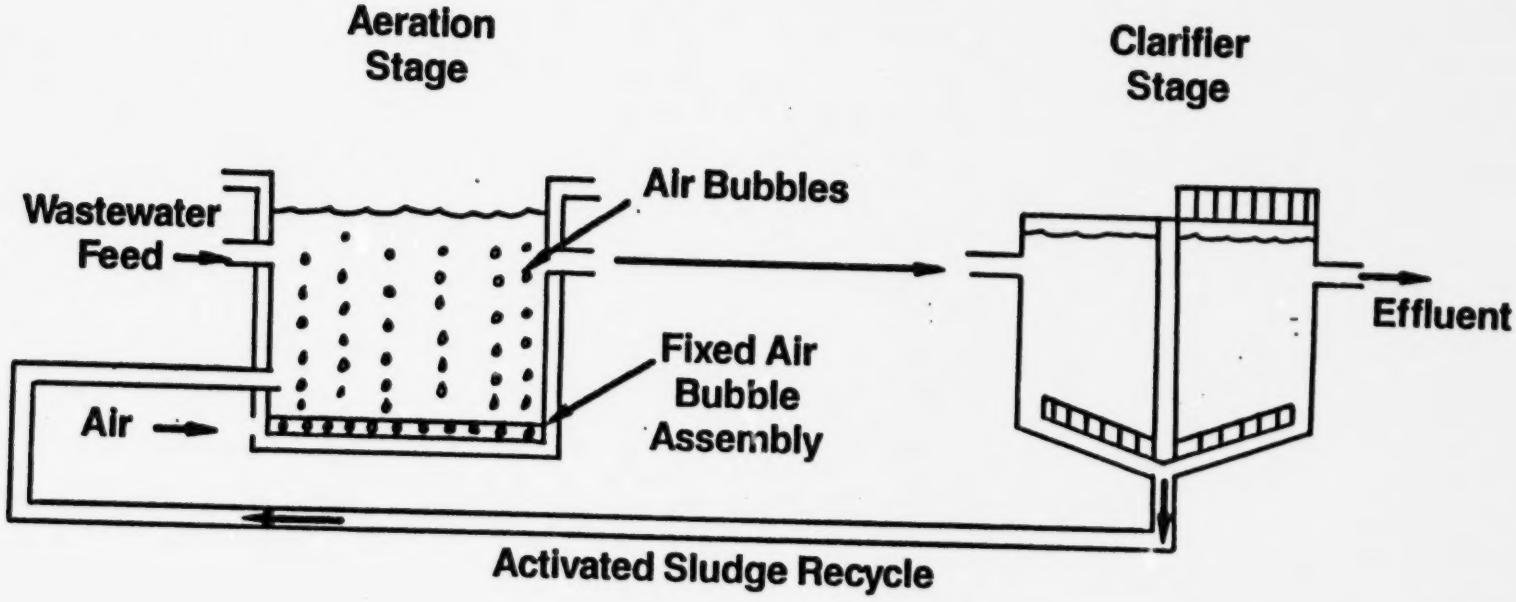


FIGURE 8.

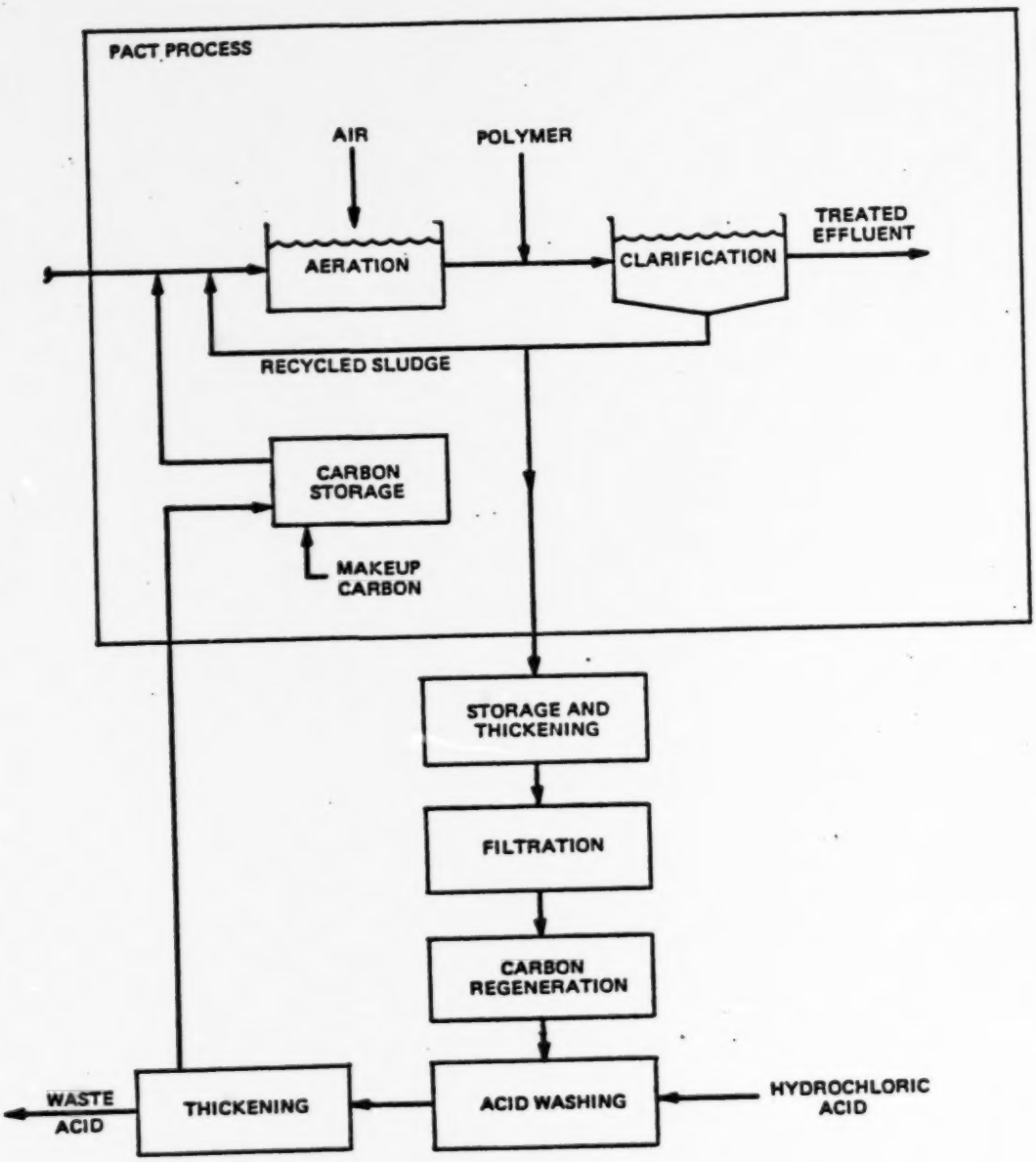
oxygen process a multi-stage, closed aeration tank is used with mechanical aerators for dissolution of the pure oxygen gas.

Another variation of the activated sludge process is the PACT (Powdered Activated Carbon Treatment) process. The PACT process involves the addition of powdered activated carbon to the aeration tank. The activated carbon and the microorganisms form a matrix, resulting in improved removal of organic matter over that of the conventional activated sludge process. The carbon adsorbs organics and acts as a weighting agent for the matrix, enhancing both the removal of adsorbable organics, regardless of biodegradability, and solids settling and thickening. Also, it improves operations by dampening periodic organic loading variations, and by adsorbing toxic and inhibitory substances that would otherwise disrupt and pass through a conventional activated sludge process. Figure 9 shows the process flow for the PACT process.

Applicability to the Treatment of Hazardous Waste --

The activated sludge process is capable of significantly reducing the concentration of a wide variety of organic compounds, including many toxic and hazardous compounds. However, only dilute aqueous wastes (<1%) can normally be treated, and most hazardous organic wastes are toxic or inhibitory to the process except at very low concentrations. Therefore, treatment of hazardous wastes by this process would be most practicable where the aqueous waste can be mixed with a more readily biodegradable wastewater stream.

The removal of toxic pollutants from aqueous wastes discharged to biological treatment systems during an extensive EPA study of the Fate of Priority Pollutants in Publically Owned Treatment Works (POTW) was very good for volatile organic, acid extractable organic, and most base neutral extractable organic compounds (EPA, 1982).



SOURCE: DUPONT

FIGURE 9. SCHEMATIC DIAGRAM OF PACT (DUPONT) PROCESS

There are no indications of any activated sludge plants designed specifically for the treatment of solvent wastes. However, because of the widespread use of these materials, they are typically present in the influent wastes to POTWs. Solvents are volatile organic compounds (VOCs) and may therefore be air-stripped or biodegraded in the activated sludge process. It is unknown what portion of the solvent is biodegraded and what portion is simply air-stripped. Data from the study cited above approximated that 65 percent of the influent VOC mass is biodegraded or stripped; 10 percent is adsorbed on the biomass and 25 percent of the total toxic VOC mass passes through the activated sludge process untreated.

Of the acid extractable fraction, phenol is the most studied compound. Coke plant wastes containing over 1,000 mg/l of phenol have been successfully treated by activated sludge to less than 0.1 mg/l in the effluent. Biodegradation removals for phenol averaged 84 percent during the previously referenced study, sorption removals via the wasting of sludge was eight percent and eight percent of the influent phenol mass was discharged in the final effluent. Although base-neutral extractable organic compounds are to an extent biodegradable, the study results suggested that 32 percent of the total base-neutral extractable compounds pass through the treatment plant in the effluent, 62 percent of the mass is partioned to the sludge stream and only six percent is biodegraded.

Toxic and hazardous metals are either concentrated in the sludge by physical mechanisms or pass through the treatment process in the soluble phase. Cadmium, zinc, copper, lead and chromium show a strong affinity for partitioning to the sludge stream, while nickel and aluminum are often soluble and less treatable.

Table 1 includes percent removals of selected toxic compounds in biological treatment plants during the Fate of Priority Pollutants in POTWs study and Table 2 includes percent removals of organic priority pollutants in biological treatment systems as observed during a number of studies.

Generally, the activated sludge process is readily capable of decomposing alcohols, aldehydes, fatty acids, alkanes, alkenes, cycloalkenes and aromatics. Other compounds such as isoalkanes and halogenated hydrocarbons are more resistant to microbial decomposition, and therefore the degreee of treatment and the rate of decomposition are dependent upon the acclimated biomass in the activated sludge system. The use of mutant bacteria has been reported to be effective for biological treatment of a hazardous waste which is relatively uniform in composition. Table 3 presents biodegradation results for one patented process (Wilkinson, 1978).

Activated sludge treatment systems are employed at several hazardous waste treatment facilities, including DuPont Environmental Services, Hyon Waste Management Services, and Bio Ecology Systems, Inc. The system at Hyon treats waste with up to 10,000 ppm chemical oxygen demand (COD) on a continuous basis and Bio Ecology handles wastes with up to 30,000 ppm COD on a batch basis (DeRenzo, 1978).

The PACT process has been in operation at the highly diverse DuPont Chambers Works since 1977. Volatile and acid extractable priority pollutant removals are generally better than 90 percent. Many difficult-to-degrade molecules, such as substituted aromatics, are readily adsorbed on activated carbon. It isn't surprising, therefore, that the PACT process consistently produces better effluent quality than activated sludge in terms of waste streams containing significant amounts of refractory organics (duPont, 1981).

TABLE 1. COMPARISON OF SELECTED TOXIC POLLUTANT PERCENT REMOVALS BY SECONDARY BIOLOGICAL TREATMENT PROCESSES[1]

Pollutant	Activated Sludge	Pure O_2 System	Aerated Lagoon	Trickling Filters	RBCs[2]
Volatile Organics					
benzene	(10) 77	(2) 87	(0) -	(1) 92	(0) -
chloroform	(20) 62	(3) 50	(0) -	(4) 69	(0) -
ethylbenzene	(10) 90	(3) 86	(1) 83	(4) 89	(0) -
methylene chloride	(14) 48	(3) 34	(1) 96	(4) 32	(0) -
tetrachloroethene	(20) 82	(3) 75	(1) 91	(4) 62	(1) 50
toluene	(21) 93	(3) 99+	(1) 89	(4) 93	(1) 99+
trichloroethene	(20) 90	(2) 67	(1) 97	(4) 95	(1) 67
1,1,1-trichloroethane	(17) 88	(3) 80	(1) 91	(3) 91	(0) -
trans-1,2-dichloroethane	(19) 80	(2) 85	(1) 88	(0) -	(0) -
Acid Extractable Organics					
phenol	(15) 89	(3) 99+	(1) 50	(3) 94	(1) 99+
Base-Neutral Extractable Organics					
bis (2-ethylhexyl) phthalate	(8) 62	(3) 64	(1) 23	(4) 72	(1) 86
butyl benzyl phthalate	(2) 94	(3) 84	(1) 93	(1) 93	(0) -
di-n-octyl phthalate	(6) 68	(1) 98	(1) 50	(3) 50	(0) -
diethyl phthalate	(2) 91	(0) -	(0) -	(0) -	(0) -
naphthalene	(6) 92	(1) 70	(0) -	(0) -	(0) -
Metals					
cadmium	(6) 85	(2) 83	(1) 44	(2) 84	(0) -
chromium	(22) 84	(3) 76	(1) 49	(4) 63	(0) -
copper	(22) 84	(3) 92	(1) 21	(4) 75	(1) 97
lead	(2) 82	(1) 97	(1) 0	(0) -	(0) -
mercury	(8) 76	(3) 83	(1) 0	(2) 49	(0) -
nickel	(15) 34	(2) 18	(1) 14	(4) 0	(0) -
silver	(5) 83	(2) 80	(1) 0	(2) 83	(0) -
zinc	(22) 81	(3) 81	(1) 51	(4) 73	(1) 81

1 Fate of Priority Pollutants in POTWS, EPA 440/1-82/303.
( ) Number in parenthesis is number of plants with one-week of analytical results included in database.
2 Rotating Biological Contactor.

TABLE 2. REMOVAL OF TOXIC ORGANIC COMPOUNDS IN BIOLOGICAL TREATMENT SYSTEMS[a]

Pollutant	Type of Treatment	Influent Level, ug/l	Percent Removal
1. Acenaphthene	AS-M	0.9	95
	AS-I (10)	15	> 84
	AL-I (1)	4.0	0
4. Benzene	AS-M	8.8	66
	AS-M	7.7	92
	AS	-	90-100
	AL	6-53	(-17)-96
	PACT	160	> 99
	AS-I (9)	10,250	> 60
	AL-I (2)	46.9	> 84
5. Benzidine	AS-I (1)	4	0
	AL-I (1)	11.9	41
6 Carbon Tetrachloride	PACT	95	94
	AS-I (2)	250	> 98
7 Chlorobenzene	PACT	1,900	99+
	AS-M	177	99+
	AS-I (6)	15.2	> 67
8 1,2,4-Trichlorobenzene	AS-M	0.6	83
	AS-I (11)	285	> 67
9. Hexachlorobenzene	AS-I (4)	0.75	> 47
	AL-I (1)	10	0
10. 1,2-Dichloroethane	AS-M	1.5	65
	AS-M	8.4	85
11. 1,1,1-Trichloroethane	PACT	18	> 99
	AS-M	88.4	70
	AS-M	1,791	98
	AS-I (6)	9.2	> 74
	AL-I (1)	550	96
13. 1,1-Dichloroethane	AS-M	1.7	6
	AS-M	6.7	92
	AS-I (2)	7.1	> 9
14. 1,1,2-Trichloroethane	AS-I (1)	11	> 9
15. 1,1,2,2-Tetrachloroethane	AS-I (2)	12.8	> 22
17. Bis (chloromethyl) Ether	AS-I (1)	59	83
18. Bis (2-chloroethyl) Ether	AS-M	0.12	92
	AS-I (1)	19	> 47
20 Naphthalene	AS	2,000	100
	AS-I (1)	2	50
	TF-I (1)	2	0
	AL-I (1)	19	> 47
21. 2,4,6-Trichlorophenol	AS-I (10)	703	36
	AL-I (1)	1,000	99
23. Chloroform	AL	425-2,645	(-1)-86
	AS-M	4.2	5
	AS-M	17.1	98
	AS-M	37.5	49
	AS-I (16)	33	> 61

TABLE 2. (Continued). REMOVAL OF TOXIC ORGANIC COMPOUNDS IN BIOLOGICAL TREATMENT SYSTEMS

Pollutant	Type of Treatment	Influent Level, ug/l	Percent Removal
23. Chloroform (cont'd)	TF-I	19	0
	AL-I (3)	531	> 36
24. 2-Chlorophenol	AS-I (2)	10	46
25-27. "Dichlorobenzene"	PACT	720	35
25. 1,2-Dichlorobenzene	AS-M	1.8	28
	AS-M	4.8	28
	AS-M	43.9	97
	AS-I (12)	28.8	> 74
	AL-I (1)	250	> 96
26. 1,3-Dichlorobenzene	AS-M	3.1	86
27. 1,4-Dichlorobenzene	AS-I (8)	30	> 82
	AL-I (1)	53	> 81
29. 1,1-Dichloroethene	AS-M	43.2	97
31. 2,4-Dichlorophenol	AS-I (2)	13.3	25
32. 1,2-Dichloropropane	AS-I (2)	16	> 67
34. 2,4-Dimethylphenol	AS-I (3)	39.7	> 32
35. 2,4-Dinitrotoluene	PACT	2,000	75
	AL-I (1)	3	0
36. 2,6-Dinitrotoluene	PACT	1,900	76
	AS-I (1)	390	0
	AL-I (1)	12	> 83
37. 1,1-Diphenylhydrazine	AS	2,000	100
	AS-I (1)	340	0
	AL-I (1)	14	0
38. Ethylbenzene	PACT	29	78
	AS-M	148	99
	AS-I (24)	882	83
	AL-I (3)	45	> 78
39. Fluoranthene	AS-M	0.6	92
	AS-I (1)	2	0
	AL-I (1)	2	0
41. 4-Bromophenyl Phenyl Ether	AS-I (1)	360	95
42. Bis (2-chloroisopropyl) Ether	AS-M	0.16	62
	AL-I (1)	2	0
43. Bis (2-chloroethoxy) Methane	AL-I (1)	25	> 60
44. Methylene Chloride	AS-M	9.0	49
	AS-M	293	0
	AS-I (5)	144	34
	TF-I (1)	1	0
	AL-I (3)	1,114	65
45. Methyl Chloride	AL-I (1)	56	> 91
47. Bromoform	PACT	910	89
	AS-I (1)	3	0
48. Dichlorobromomethane	PACT	54	> 99
	AS-I	5.8	0

TABLE 2. (Continued). REMOVAL OF TOXIC ORGANIC COMPOUNDS IN BIOLOGICAL TREATMENT SYSTEMS

Pollutant	Type of Treatment	Influent Level, ug/l	Percent Removal
49. Trichlorofluoromethane	PACT	920	99
	AS-I (5)	556	19
	TF-I (1)	48	> 79
51. Chlorodibromomethane	PACT	81	>99
54. Isophorone	AS-I (2)	10	> 10
	AL-I (1)	3.0	33
55. Naphthalene	AS-M	1.3	35
	AS-M	10.9	62
	AS-I (26)	50	> 64
	TF-I (1)	55	0
	AL-I (2)	14.1	> 29
	TL-I (1)	56	56
56. Nitrobenzene	AL-I (1)	10	0
57. 2-Nitrophenol	AS-I (1)	40	> 99
58. 4-Nitrophenol	PACT	56	> 99
	AS-I (1)	90	> 99
	AL-I (1)	13	23
60. 2,6-Dinitro-o-cresol	PACT	11	99
61. Nitrosodimethylamine	AS	2,000	> 95
62. N-Nitrosodiphenyl Amine	AS-I (2)	5.3	> 84
	AL-I (1)	3	67
63. N-nitrosodi-n-propylamine	AS-M	0.5	88
	AS-M	6.7	99
	AS-I (2)	11	0
64. Pentachlorophenol	AS-I (15)	5,333	> 70
	TF-I (1)	3	0
	AL-I (1)	34	> 71
65. Phenol	TF	105	91
	AS	105	> 99
	PACT	440	96
	AS-I (30)	335	> 77
	TF-I (1)	37	0
	AL-I (3)	25.4	> 41
66. Bis (2-ethylhexyl) Phthalate	PACT	2.4	67
	AS-M	1.3	31
	AS-M	50	78
	AS-I (38)	102	37
	TF-I (1)	35	83
	AL-I (5)	37	> 70
	TL-I (2)	26	> 58
67. Butyl Benzyl Phthalate	AS-M	18	91
	AS-I (1)	11	0
	AL-I (1)	6	0
68. Di-n-butyl Phthalate	AS-M	5.6	68
	AS-M	13	62
	AS-I (9)	23	> 60

TABLE 2. (Continued). REMOVAL OF TOXIC ORGANIC COMPOUNDS IN BIOLOGICAL TREATMENT SYSTEMS

Pollutant	Type of Treatment	Influent Level, ug/l	Percent Removal
68. Di-n-butyl Phthalate (cont'd)	TF-I (1)	15	25
	AL-I (1)	1	0
69. Di-n-octyl Phthalate	AS-I (1)	5,000	0
70. Diethyl Phthalate	AS-M	6.6	98
	AS-M	1.4	79
	AS-I (17)	15	56
	TF-I (1)	140	0
	AL-I (1)	4	0
71. Dimethyl Phthalate	AS-I (9)	60	60
	AL-I (1)	8	25
73. Benzo(a)pyrene	AL-I (1)	3	33
77. Acenaphthene	AS-M	0.2	80
	AL-I (1)	5	0
78. Anthracene	AS-I (7)	8.5	> 60
80. Fluorene	AS-M	1.7	94
	AS-I (2)	2	> 99
81. Phenanthrene	AS-M	3.2	91
	AL-I (1)	3	0
84. Pyrene	AS-I (5)	2.3	16
	AL-I (1)	3	67
85. Tetrachloroethene	PACT	62	88
	AS-M	6.4	0
	AS-M	49	80
	AS-M	560	> 99
	AS-I (11)	25.6	> 75
	AL-I (1)	25	> 60
86. Toluene	PACT	680	> 99
	AS-M	70	> 99
	AS-M	112	99
	AS-I (31)	119	52
	AL-I (3)	143	> 93
87. Trichloroethene	AL	10-120	(-23)-73
	PACT	60	90
	AS-I (12)	31.3	68
	TF-I (1)	1	0
89. Aldrin	AS+MMF	-	100
90. Dieldrin	AS+MMF	-	72
92. DDT	AS+MFF	-	100
93. DDE	AS+MMF	-	39
94. DDD	AS+MMF	-	100
	AS-M	0.3	37
	AS-M	0.17	17

TABLE 2. (Continued). REMOVAL OF TOXIC ORGANIC COMPOUNDS IN BIOLOGICAL TREATMENT SYSTEMS

Pollutant	Type of Treatment	Influent Level, ug/l	Percent Removal
100. Heptachlor	AS-I (1)	6.3	76
104. Lindane	AS+MMF	-	0

a. From J.W. Patterson, P.S. Kodukala, Chemical Engineering Progress, April 1981.

( ) Numbers in parenthesis represent number of treatment plants for which data were averaged.

AS - Activated Sludge; M - Municipal Facility; I - Industrial Facility; AL - Aerated Lagoon; TF - Trickling Filter; MMF - Mixed Media Filtration; PACT - Activated Sludge with Powdered Activated Carbon added, patented duPont process; TL - Tertiary Polishing Lagoon.

TABLE 3. BIODEGRADATION ABILITY TO PHENOBAC™ AT 30°C (86°F)

Compound and procedure	Initial Concentration (mg/l)	Percentage destruction	Treatment time (hr)
Halophenols (mutant pseudomonas, activated sludge)			
phenol	500	100	10
2,4-dichlorophenol	200	100	35
pentachlorophenol (PCP)	200	26	120
2,3,5-trichlorophenol	200	100	55
Aryl Amines (mutant aerobacter, oxidation lagoons)			
o-dianisidine	500	100	40
m-toluidine	500	100	10
2,4,6-trichloroaniline	500	100	30
aniline	500	100	15
Aryl Halides (mutant pseudomonas, biological filter/activated sludge)			
1,2,4,5-tetrachlorobenzene	200	80	120
1,3,5-trichlorobenzene	200	100	50
m-dichlorobenzene	200	100	30
hexachlorobenzene	200	0	120

Source: Wilkinson, R.R., G.L. Kelso, F.C. Hopkins; 1978.

Environmental Considerations --

The major residuals from the activated sludge process are waste activated sludge and the treated effluent. In addition, aerosols are generated and volatile materials may be stripped by the aeration process.

As noted earlier, several mechanisms are involved in removal of toxic and hazardous compounds in the activated sludge process. In addition to biodegradation, the material may be removed by air-stripping, and/or sorption/sedimentation to the sludge stream. Small droplets of the mixed liquor may become airborne especially where surface aeration is used. The environmental effects of these removal mechanisms are important considerations since they represent a transfer of the toxic/hazardous materials from the aqueous environment to the atmosphere and land if the sludge is landfilled.

2. Trickling Filter

Process Description --

The trickling filter process is an aerobic attached growth biological treatment process which removes organic matter from aqueous waste streams. The wastes are distributed over and allowed to trickle through a fixed bed of rocks or synthetic media that has attached microbial growth. The organic material present in the wastewater is degraded by a population of microorganisms attached to the filter media. As the microorganisms on the filter media grow, the thickness of the slime layer increases such that an anaerobic environment is established near the surface of the media. Thus, the biological treatment afforded encompasses both aerobic and anaerobic degradation. The operation of the trickling filters typically includes the recycling of a portion of the filter effluent and settled secondary sludge (if applicable) in order to increase the net contact time of the waste with the attached biological mass.

Applicability to the Treatment of Hazardous Waste --

Trickling filters are applicable to treatment of the same types of hazardous wastes that are treatable by activated sludge, i.e. aqueous wastes containing organics, including solvents and halogenated organics that are biodegradable. As with activated sludge, mixture of the hazardous waste stream with a wastewater containing more readily degradable organic material may be required for stable operation. The efficiency is comparable to that of activated sludge systems as shown in Tables 1 and 2. The process is more resistant to shocks and therefore can be effective as a "roughing" or pretreatment unit prior to other treatment processes. The resiliency of the trickling filter to handle variations in organic and hydraulic loadings in conjunction with its limited operational flexibility, results in this process being used frequently as a pretreatment unit before activated sludge systems in industrial treatment applications.

Environmental Considerations --

Trickling filter treatment plants are capable of removing toxic and/or hazardous compounds from aqueous hazardous waste discharged to these unit processes by means of biodegradation and/or sorption on the sludge. Air-stripping is a very minor phenomenon that may occur as the aqueous waste is dispersed over the filter media, however, it is not a dominant factor. Accumulation of heavy metals and high molecular weight organics in the humus or sludge are comparable to that of activated sludge plants.

3. Rotating Biological Contactor

Process Description --

The rotating biological contactor (RBC) is an attached growth biological treatment process reactor applicable to aqueous wastes. The contactor consists

of a series of closely spaced circular disks of polystyrene, polyvinyl chloride or similar materials. Initially, the disks are partially submerged in the waste and slowly rotated until an attached microbial growth of a uniform thickness of two to four mm thick is developed. Continued operation of the disks alternately contacts the microbial growth with the organic material in the waste and then with the atmosphere for adsorption of oxygen. This motion maintains the biomass in an aerobic condition.

The rotating action of the contactor also causes sloughing of excess biological material from the disks. This material is then seperated out in a clarifier following the RBC basin. Figure 10 depicts a typical RBC.

Applicability to the Treatment of Hazardous Waste --

Rotating biological contactors can be used for treatment of dilute aqueous wastes containing biodegradable organics including solvents and halogenated organics. The large amount of biological mass permits the system to withstand organic and hydraulic surges effectively.

Like other biological treatment processes, rotating biological contactors are applicable only to relatively dilute aqueous wastes, and are inhibited or ineffective at high concentractions of heavy metals, refractory organics and other "toxic" conditions. Therefore, mixing of an aqueous hazardous waste with another waste stream containing readily biodegradable material may be required.

Environmental Considerations --

Given the proper acclimated biomass, temperature and nutrients, RBCs are capable of yielding effluents relatively free of toxic compounds. As previously mentioned, this process does yield sludge as a byproduct, and the accumulation of heavy metals and certain refractory organic compounds that may render this sludge hazardous must be evaluated. The continuous agitation of the waste by

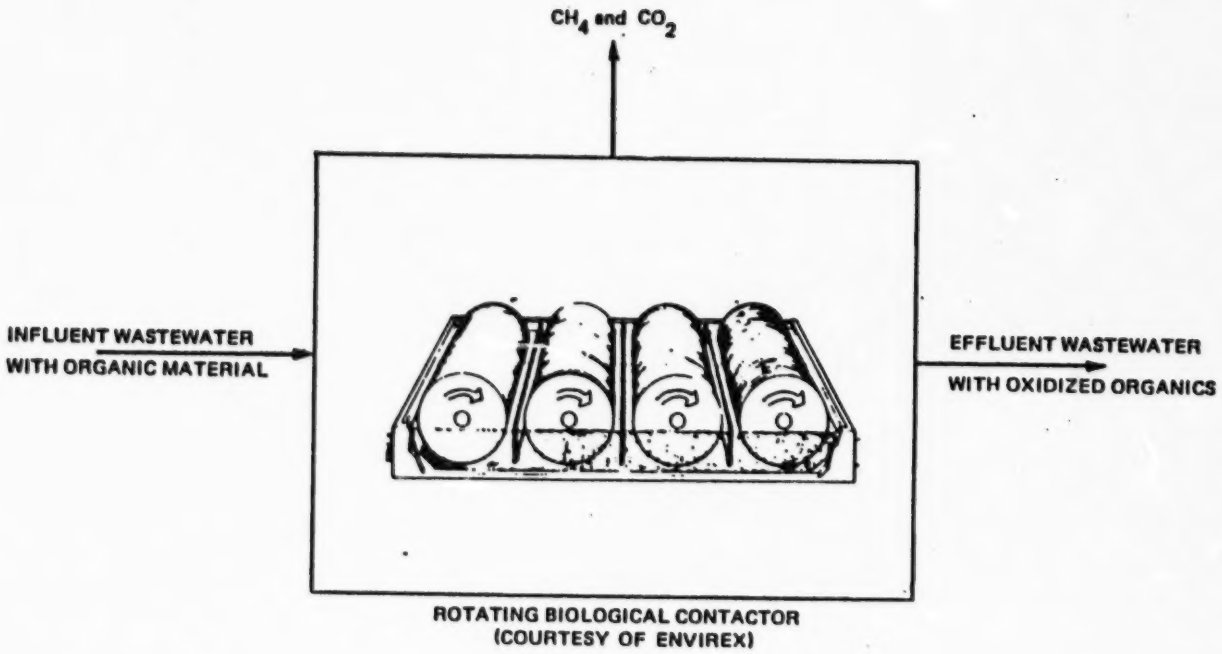


FIGURE 10. SCHEMATIC OF ROTATING BIOLOGICAL CONTACTOR

the disks can result in certain VOCs being stripped from the waste environment. The concentration of these compounds in the atmosphere in the immediate vicinity of the RBC basin may be important especially where the system is enclosed, as is often the case in cold climates.

SECTION III

EMERGING ALTERNATIVE TECHNOLOGIES FOR HAZARDOUS WASTE TREATMENT

A. PHYSICAL TREATMENT

1. Metal Binding Compounds

Process Description --

Tailor-made synthetic molecules which mimic those metal-capturing compounds found in living cells are covalently bonded to a substrate such as silica gel. By altering the structure of the molecules, they may be made to selectively remove certain heavy metal ions from a solution containing alkali metal ions, letting the latter pass through the system. An example of this selectivity is the case where 670 ppm cadmium in tap water was reduced to 67 ppb (the limit of detection).

The compounds are generally insoluble organic sideophores such as N-substituted hydroxamates, phenolates, and catecholates, bonded to activated silica gel particles; in some instances polyacrylamide is the carrier. Proper selection of carrier and composition bonded to it allows construction of packed columns through which the metal bearing water is passed. After the compositions have been saturated with metal ions, they may be regenerated with dilute hydrochloric acid; only 2 to 3 bed volumes are required to elute the metal.

Applicability to the Treatment of Hazardous Waste --

Metal binding compounds may be used to remove toxic heavy metals from plating rinse waters, leachate from landfills, mine drainage waters, and others where the metal concentration is too low to be treated by conventional methods. High concentrations of metals are more economically removed by more conventional methods such as liquid ion exchange, reverse osmosis, or ion exchange resins.

Environmental Considerations --

The reject stream from this treatment is a relatively concentrated heavy metal solution. In many cases the metal may be recovered, in others neutralization and disposal may be preferred.

2. Microwave Discharge

Process Description --

High-frequency microwave power is used to establish a plasma or gaseous discharge in which neutral molecules are partially decomposed into metastable, atomic, free radical and ionic species. The decomposition products typically recombine to form a variety of stable molecules, some of higher molecular weight and of higher toxicity than this feed. Plasmas may be initiated in low-pressure gases of all kinds, and solids and liquids exposed to the reactive species in plasmas generally undergo chemical change. Toxic vapors and liquids introduced into an oxygen plasma undergo reactions similar to those of incineration, but at much lower temperatures. To date, solids have not been treated by this technology and, in general, it is only practical to treat vaporizable compounds. The reason for this is that reduced pressures (4,000 to 11,000 Pa)* are required to allow free electrons to be accelerated to energy levels high enough to dissociate a molecule or fragment on collision.

If oxygen is passed through the plasma, atomic oxygen becomes a primary reactive species which rapidly oxidizes the organic compounds introduced into the discharge. In addition, the large number of energetic free electrons continually bombard the organic molecules or fragments and any remaining organic species are broken up into small free radical fragments that rapidly react with the oxygen free radicals present.

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*1 Pa = 9.89923 x 10-6 Atm

Applicability to the Treatment of Hazardous Waste --

Microwave discharge may be used to treat hazardous organic wastes with boiling points below their decomposition temperatures. Experimental reactors have destroyed vinyl bromide, aniline 1,1,1-trichloroethane, and carbon tetrachloride. The process should be considered for small quantities of highly toxic materials which cannot be handled by any other means, or for recovery of high value components, as destruction costs are estimated at $1.00/lb.

Environmental Considerations --

The high degree of destruction yields off-gases that are quite innocuous.

3. Photolysis of Hazardous Chloroaromatic Compounds

Process Description --

Photodegradation studies employing both natural sun light and artificial lights have been carried out in the gas phase, in solution employing water and organic solvents, and in the solid state as thin films on glass plates or adsorbed on soil or silica. Chemicals of interest which have been demonstrated to undergo photodecomposition include DDT, the polychlorinated biphenyls (PCBs) and the chlorodibenzo-p-dioxins (CDDs). The most relevant processes currently proposed for hazardous waste detoxification are solution and solid phase photodecomposition.

In solution phase work, various groups have studied the effects of wavelength of light using artificial illumination sources as well as the effects of polar and nonpolar solvents and photosensitizers. In general, it can be stated that a photolytic reaction carried out in a polar solvent will yield a product where the chlorine has been replaced by a hydroxyl group whereas in nonpolar solvents reductive dechlorination products predominate. The solution phase photodechlorination of hazardous waste streams and/or hazardous waste lagoons

has been proposed and in some cases applied. In these techniques a hazardous waste stream is pretreated, if required, to remove interfering contaminants, e.g., those which would quench the wavelenghts of interest or otherwise block light transmission, and then sent through a batch or continuous flow photolytic reactor.

The basic components of a flow or batch photochemical reactor would consist of inlet and recirculation pumps, valves, associated plumbing and the reactor proper which usually is a water-cooled, low pressure mercury lamp source enclosed in quartz glass. Ports for sampling inlet and outlet liquid streams would be required as well as rapid analytical monitoring methods for determination of chemical products or starting material(s).

The solid phase photodecomposition of chloroorganics on soils and surfaces has in recent times drawn much attention as a potential detoxification method especially with regard to destruction of 2,3,7,8-TCDD and other chlorodioxins. Here again natural sunlight and artificial light(s) in conjunction with hydrogen donors applied to the contaminated area have been investigated and are still under consideration. A major drawback in soil treatment via photolysis is obviously the lack of penetration depth of ultraviolet radiation. Soil or ground-turning by means of cultivators has been suggested and attempted in some cases as a method for exposing the contaminated material to UV light. Treatment of contaminated surfaces not exposed to sunlight has been attempted with banks of low pressure mercury lights again in conjunction with a surface pretreatment consisting of application of a hydrogen donor. These methods initially were investigated in Italy in the Seveso area.

Applicability to the Treatment of Hazardous Waste --

Though extensively studied in laboratory-scale investigtions for both hazardous waste decontamination and novel organic reactions, pure photolysis has some major drawbacks such as high energy usage and limitations in treatability of bulk liquid streams. A further drawback is lack of understanding of reaction mechanisms associated with both solution and solid phase photolysis. A combination of UV/ozonation and UV/chlorination has been applied to pilot and full scale applications in the hazardous waste area.

Environmental Considerations --

A variety of products can be obtained by photolytic reactions. In the photolysis of 2,3,7,8-TCDD and other chlorodioxins, a totally dechlorinated dibenzo-p-dioxin can be produced but generally a mixture of partially dechlorinated products is the result. From a toxicological view, each product must be investigated with respect to health and environmental effects. The application of photolysis as a solution to particular decontamination problems must be taken on a case by case basis.

4. Reversible Gel Extraction

Process Description --

Reversible gels are prepared by the polymerization of acrylamide in water solution with bisacrylamide added as a crosslinking agent. The resulting gel is colorless, transparent, soft and elastic with a slippery or slimy surface. The gels are then placed in a basic solution for up to 60 days to hydrolyze approximately 25% of the $CONH_2$ side chains to COOH. The gel will now undergo a large size change, similar to a phase change, when it is exposed to a slight change in the pH of a solution that it is placed in.

A second type of gel can be prepared by polymerization of acryldiethylamide with bisacrylamide as a crosslinking agent with no subsequent hydrolysis step. This gel will undergo a large size change with slight changes in the temperature of the surrounding solution. The gels are normally prepared in water solution in their "expanded" form.

The pH sensitive gels and the temperature sensitive gels can increase their size by a factor of from 10 to 50 times their collapsed size. If a collapsed gel is placed in a solution of dilute aqueous waste, the gel can be made to change phase by either pH or temperature change, and the gel will expand, extracting water from the dilute waste, excluding and concentrating the hazardous material in the remaining solution. The surface of the gel is a highly crosslinked polymer web which acts as a filter for the pollutant as water is absorbed into the gel and thus the gel is more effective in removing larger, higher molecular weight pollutants.

When the gel has expanded, it is removed from the waste stream and regenerated by either pH or temperature, which collapses the gel and releases the absorbed water. The size change ratio that can be achieved with the gel is inversely proportional to the concentration of pollutants and other dissolved material such as salts in the waste stream.

Applicability of the Treatment of Hazardous Waste --

The gels are now being investigated in the laboratory for general operating characteristics and removability of several pure compounds. There is currently no data on applicability to actual industrial waste. However, the laboratory study indicates that the gels are most effective in removing large solute molecules having molecular weights of 1500 or more and colloids.

Environmental Considerations --

The reversible gel extraction process produces a more concentrated waste which requires additional treatment and must be disposed.

B. CHEMICAL TREATMENT

1. Hydrolysis

Process Description --

Hydrolysis formally refers to the reaction of water or related species with an organic or inorganic compound.

$$R\text{-}X + H_2O \text{ ----> } R\text{-}OH + HX$$

-where R is either organic or inorganic

The hydrolysis reaction generally ocurrs with a net exchange of some leaving group. The reaction can involve both anionic and cationic intermediates depending on the pH. Specific ion catalysis describes the reaction conditions when the rate of hydrolysis is catalyzed by either the hydronium ion H_3O+ or the hydroxyl ion OH^-. Due to the steady state of the water concentration in most environmentally significant hydrolysis reactions, the pseudo first order rate constant is used to describe hydrolysis reaction as a function of pH. Most graphs depicting the hydrolysis pseudo first order rate constant vs. pH show one or more areas where multiple rate processes contribute to the overall hydrolysis rate.

The comparison of pH - rate profiles for several closely related classes of hydrolyzable compounds can show that chemicals of different structure respond to acid or base promotion of the hydrolysis reaction in a variety of ways. For instance the rate of hydrolysis for alkyl halides spans six orders of magnitude between methyl fluoride and t-butyl chloride. Esters and amides exhibit significant differences in the rate constant depending on the steric

and electronic properties of the substituent groups attached to the organic moiety. Generally, esters hydrolyze about 1,000 times faster than the corresponding amide at the same pH. Half lives for hydrolyzable chemicals at neutral conditions and room temperature (pH 7 and 25°C) range from several hundred centuries to only a few minutes.

Temperature plays an important role in the determination of the rate. Using the Arrhenius form of the rate expression for a hydrolysis reaction, the temperature dependance of the rate is roughly a doubling of the rate for every 10°C change in temperature.

The effects of ionic strength on hydrolysis reactions are difficult to predict. Both acceleration and deceleration of the rate has been observed depending on the substrate, the specific salts and their concentrations. Salt effects of this kind are associated with changes in the activity coefficients of ionic and polar species or transition states with significant charge separation; no bond making or breaking is involved in such interactions.

The addition of solvents to the hydrolysis medium can drastically affect the rate of reaction. The true meaning of pH in such mixed solvent systems becomes questionable and requires at times a form of double extrapolation to conditions of pH in water as the sole solvent.

A number of alkaline and heavy metal ions catalyze the hydrolysis of a variety of organic esters. The metal ion appears to increase the effective concentration of hydroxyl ion at pH levels where its concentration would otherwise be negligible. This explanation serves to describe only one facet of this complex behavior.

Applicability to the Treatment of Hazardous Waste --

Most work on hydrolysis reactions reported as occuring in the environment have been carried out in natural waters. Methoxychlor in buffered waters and

two natural waters was found to have a half-life of 3.7 hr. Among other compounds studied in natural waters are 2,4-dichlorophenoxyacetic acid, malathion, parathion, methyl parathion, Zectran(4-diamethylamion-3,5-xylyl methyl carbamate) and Sevin(N-methyl-1-napthyl carbamate). All of these compounds have easily hydrolyzable functional groups.

It appears that only ionic concentration, temperature and pH will affect the rates of hydrolysis in most natural waters. Similarly, the concentration of inorganic salts in most aquatic environments are usually too low to have any effect. Kinetic analysis of several metal ion catalyzed reactions indicates that at the concentrations of copper and magnesium ions found in aquatic or soil systems, the contributions of these reactions to the total rate of hydrolysis would be negligible.

Hydrolysis represents a potent means to convert hazardous waste to less toxic forms despite the modicum of success in the natural setting. A correctly designed control technology can easily make use of various chemical settings employing the common ion effect, metal ion catalysis, ionic strength, buffer salts and possibly alternative solvent compositions.

Environmental Considerations --

Hydrolysis reactions provide expedient and environmentally benign means to detoxify a wide range of organic and inorganic chemical species. An easy gauge to monitor the potential utility of a hydrolysis reaction for the detoxification is the bond strength of the bond subject to hydrolysis. The stronger the bond, the less likely hydrolysis is useful as a treatment technology. Basically, hydrolysis is a chemical transformation to a substrate molecule which changes the identity, physical properties and toxicity of the starting material.

2. Dechlorination Processes

Process Description --

Dechlorination processes use chemical reagents to remove chlorine from chlorinated molecules, to break apart chlorinated molecules, or to change the molecular structure of the molecule. Metallic sodium is typically the reagent used to strip the chlorine away from constituents to form sodium chloride. Other proprietary reagents are often used in conjunction with metallic sodium to further treat the dechlorinated constituents. The majority of the dechlorination research has been aimed at the detoxification of polychlorinated biphenyls (PCBs). This research is applicable to many chlorinated organic molecules. For example, this research is also appropriate for the detoxification of 2,3,7,8-tetrachlorodibenzo-p-dioxin (referred to as dioxin).

A number of companies and research institutions have investigated dechlorination processes. Four of the more common dechlorination technologies include the Acurex process, APEG process, PPM process, and Sunohio PCBX process. These processes have been found effective in reducing the toxicity of PCBs and other chlorinated organics.

The Acurex process uses a sodium reagent with a proprietary constituent. The treatment stream is filtered prior to further treatment. After filtration, the stream is transfered to a reaction tank where it is mixed with the sodium/proprietary constituent mixture. The products of this reaction are a sodium hydroxide stream and another non-toxic effluent. The Acurex reaction process is performed under a "nitrogen blanket" so that air emissions are minimized. A schematic of this process is presented as Figure 11.

The Sunohio PCBX process, unlike the Acurex process is a continuous treatment operation. This process uses a proprietary reagent to convert the PCB molecules to metal chlorides and polyphenyl compounds.

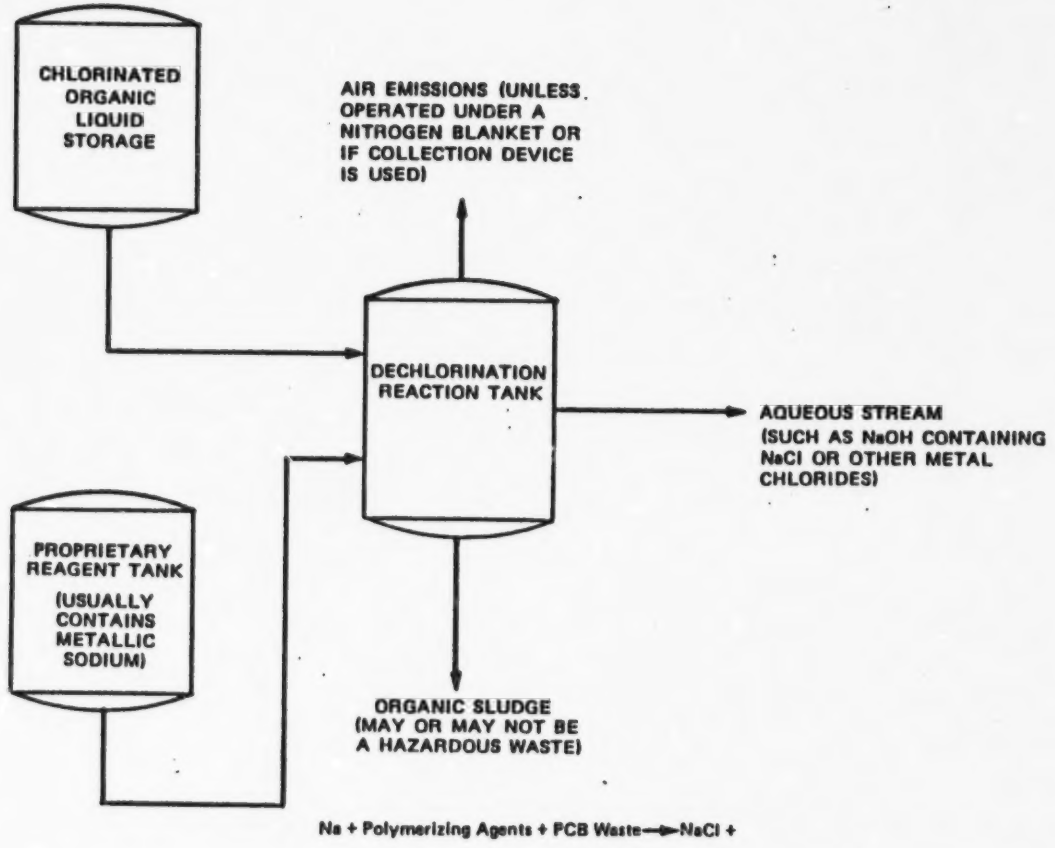

CHLORINATED ORGANIC LIQUID STORAGE
AIR EMISSIONS (UNLESS OPERATED UNDER A NITROGEN BLANKET OR IF COLLECTION DEVICE IS USED)
DECHLORINATION REACTION TANK
AQUEOUS STREAM (SUCH AS NaOH CONTAINING NaCl OR OTHER METAL CHLORIDES)
PROPRIETARY REAGENT TANK (USUALLY CONTAINS METALLIC SODIUM)
ORGANIC SLUDGE (MAY OR MAY NOT BE A HAZARDOUS WASTE)
Na + Polymerizing Agents + PCB Waste → NaCl +

FIGURE 11. SCHEMATIC OF A DECHLORINATION PROCESS

The PPM process uses a proprietary sodium reagent to dechlorinate organic molecules. This process is a batch process. A solid polymer is generated from the reaction and this substance, although regulated, can be more easily disposed than the chlorinated organics.

The APEG process uses polyethylene glycols or their derivatives that have been reacted with alkali metals or their hydroxides. Dioxin and PCBs can be destroyed in soil using a series of reagents prepared from potassium and polyethylene glycols (KPEG), however, moisture adversely influences the rates of reaction. A heated slurry process has subsequently been developed to negate the influence of moisture. This is a batch process that is controlled at operating temperatures ranging from 75° to 150°C. The reaction products associated with this process include potassium chloride, non-toxic organics, and other dechlorinated materials.

Applicability to the Treatment of Hazardous Waste --

The above described processes are applicable to many chlorinated organics, such as PCBs, dioxins, solvents, and pesticides. In addition, these processes may be suitable for the treatment of other halogenated organics.

The Acurex process has been tested for removal of chlorinated carbon wastes from soils. A commercial unit designed to treat soil is in the early stages of development (GCA, 1984b). In transformer oil, 2,3,7,8-TCDD has been reduced from 200-400 ppt to 40 $\pm$ 20 ppt using the Acurex process. This system cannot be used on aqueous streams.

The Sunohio PCBX process has reduced PCB contamination in transformer oil from 225 ppm to 1 ppm PCB in one pass through the system. It is believed that, by passing the oil through the system three times, PCBs can be reduced from 3000 ppm to below 2 ppm. This process was used at a number of sites, including

Maxwell Laboratories in San Diego, where 163,000 gallons of PCB contaminated oil were processed, and Chevron in El Segundo, CA, where a total of 5,250 gallons of oil initially containing 420 ppm to 1500 ppm PCBs were processed.

The PPM process has reduced the PCB concentration in contaminated oil from 200 ppm to below detection levels. This process cannot be used on aqueous wastes.

The APEG process has been tested in the laboratory on 2,3,7,8-TCDD contaminated soils. In a laboratory-scale slurry process, 250g of PCDD or PCB contaminated soil (2000 ppm) is placed in a 1-liter reactor along with 250g of KPEG reagent. PCDDs or PCBs in the reactor are reduced to below 1 ppb after heating to 75°C with mixing for 2 hours. The reagent (>90%) is removed for reuse. A 1-10 ton/day slurry process is being prepared for field verification on actual waste sites.

Environmental Considerations --

The residues produced depend on which dechlorination process is used. The residues may or may not be hazardous. Residues from the Acurex process include sodium chloride in sodium hydroxide solutions. The Sunohio PCBX process produces polyphenyl salts. The PPM process produces a solid polymer (on the average about one 55-gallon barrel for every 10,500 gallons of oil treated). This polymer is regulated and therefore must be properly managed. The APEG process produces sodium chloride and nontoxic organics. Residues from each of the processes must be properly disposed.

3. Supercritical Fluid Extraction

Process Description --

As in liquid-liquid extraction, an organic-containing aqueous feed is contacted with a solvent in a counter-current extraction column. The solvent

is CO_2, either supercritical fluid or near-critical liquid, and the feed is an aqueous solution of organics. The resulting extract, solute in solvent, is reduced in pressure and sent to a solvent-stripping system at 40-50 atm. A CO_2 vapor stream is recovered overhead and the bottom is substantially enriched in the extracted organic.

The CO_2 vapor from the still is compressed adiabatically to extractor pressure (65 atm), increasing its temperature. From this higher temperature, heat is released by cooling and condensing the vapor in the reboiler tubes to boil-up the reboiler bottoms, and the condensed CO_2 is returned as solvent recycle to the extractor.

The product stripped of most of the CO_2 solvent is let down in pressure in sequential flashes. The raffinate is similarly flashed, and CO_2 is recovered from both streams, recompressed, and returned to the solvent system.

A qualitative comparison can be made with two major established separation processes: distillation and normal-liquid solvent extraction. Distillation or stripping is used for separating a range of organics from water, where such organic chemicals are manufactured in aqueous systems. Examples include volatile alcohols, ketones and the like (VOC's), which are high-volume solvents and chemicals. Other examples include heavy, high-boiling liquids from which water must be distilled. In both examples, distillation energy requirements are substantial. In normal-liquid solvent extraction, the extraction unit has minimal energy requirements. However, there is a need to separate solvent from extracted solute, and this is generally done by distillation. Such distillations normally require vaporization of the entire solvent volume, involving mixtures with low relative volatility and high heat of vaporization, and thus high energy costs.

Several additional benefits arise from the favorable kinetic properties of critical fluids as solvents, which may be important factors in improving process economics. The low viscosities of the solvent streams reduce pressure drops, and thus pumping requirements. Improved diffusion characteristics can lead to higher separation efficiencies in mass transfer equipment, often reducing the volume and cost of such equipment.

Applicability to the Treatment of Hazardous Waste --

Feeds to the extraction process can consist of aqueous solutions of organics, such as volatile organic compounds (VOC's), or mixtures of oil, water, and sediments. In the former case, the process yields an organics concentrate; it may have value as recycle chemicals, depending on purity, or as a fuel component. Alternatively, it can be sent to a destruction unit, now as a highly concentrated feed of hazardous material. The aqueous effluent from the unit can be extracted to sufficiently low concentrations of hazardous solute to allow discharge, or further treatment economically.

For oily emulsions, the extract may be suitable as fuel; wastes from petroleum production and refining are particularly good candidates in this regard. Sediments should typically carry through the treatment system with the water phase, for subsequent separation or discharge.

Environmental Considerations --

The supercritical fluid extraction process produces a concentrated waste which requires additional treatment and must be disposed.

4. Supercritical Water Oxidation

Process Description --

Supercritical water oxidation is the destruction of refractory organic compounds using supercritical water at a temperature and pressure of at least

374.2° C and 218.3 atmospheres, respectively. It is a developing technology which takes advantage of the greatly increased solubility of immiscible organics in water when an aqueous mixture reaches the supercritical state. Chlorinated pesticides and other high molecular weight organic compounds are reported to be completely oxidized to CO_2, H_2O, and inorganic salts under these conditions (Josephson, 1982). This reaction has been performed in a pressurized reactor as shown in Figure 12. Heat released by the oxidation of the wastes precipitates out inorganics, which become very insoluble under supercritical conditions. A portion of the supercritical effluent is recycled back to preheat the incoming feed (Josephson, 1982).

Applicability to the Treatment of Hazardous Waste --

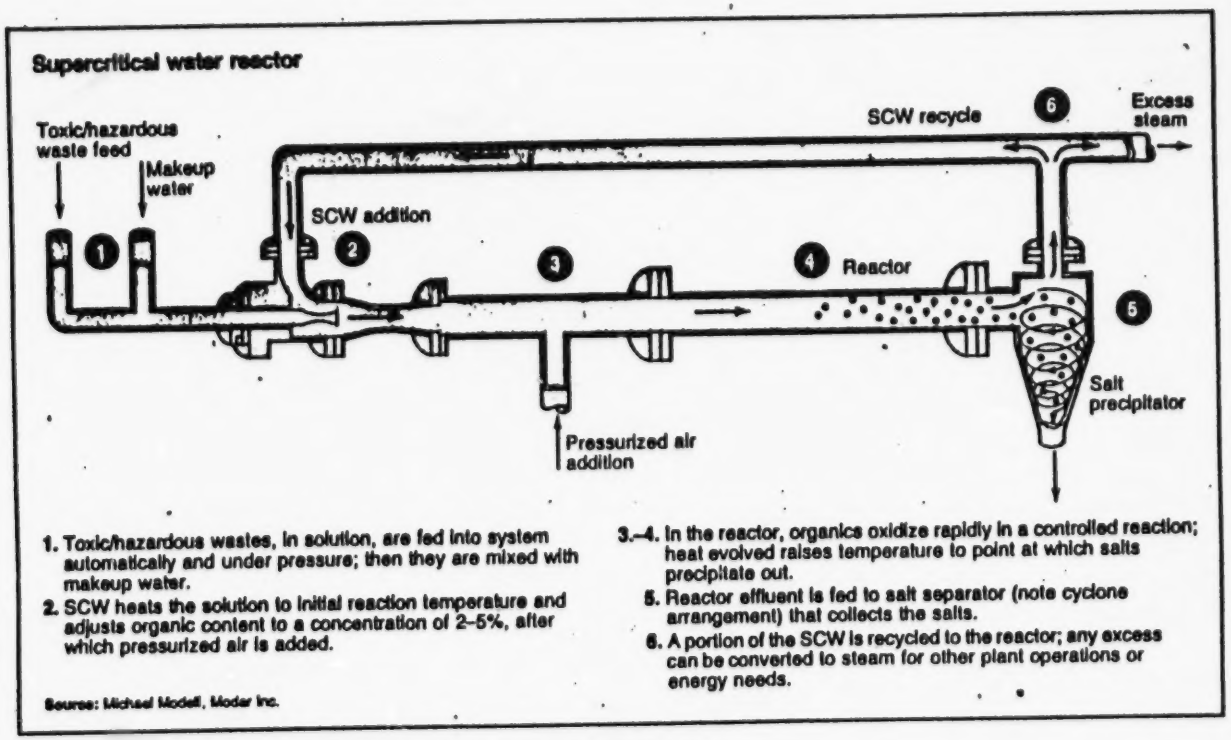
This process has been tested on a trial basis with a variety of organics by Modar, Inc. (Natick, Massachusetts). they have constructed a 50 gallon per day trailer-mounted mobile reactor and are currently designing a commercial-scale system.

Application of this technology to the following wastes seems possible once a commercial-scale facility begins operation:

- refractory organics including solvents, chlorinated pesticides and dioxins
- cyanides

Oxidation of refractory organics appears very high with a residence time of only one minute. Confirmation of these results awaits development and testing of a commercial-scale system.

The limitation of this process is that no commercial-scale supercritical unit is currently operating. Until such time as an installation becomes operative and destruction efficiencies and system reliability are verified this technology must be viewed as experimental.


Supercritical water reactor
Toxic/hazardous waste feed
Makeup water
SCW addition
SCW recycle
Excess steam
Reactor
Salt precipitator
Pressurized air addition
1. Toxic/hazardous wastes, in solution, are fed into system automatically and under pressure; then they are mixed with makeup water.
2. SCW heats the solution to initial reaction temperature and adjusts organic content to a concentration of 2–5%, after which pressurized air is added.
3.–4. In the reactor, organics oxidize rapidly in a controlled reaction; heat evolved raises temperature to point at which salts precipitate out.
5. Reactor effluent is fed to salt separator (note cyclone arrangement) that collects the salts.
6. A portion of the SCW is recycled to the reactor; any excess can be converted to steam for other plant operations or energy needs.
Source: Michael Modell, Modar Inc.

(REPRODUCED FROM ENVIRONMENTAL SCIENCE AND TECHNOLOGY
16(10) 1982, PP 548a-551A

FIGURE 12. SUPERCRITICAL WATER REACTOR

Environmental Considerations --

Inorganic salts, e.g. NaCl from chlorine in pesticides, results from oxidation of many organics with this process. These wastes will require disposal, though not necessarily as hazardous wastes.

C. BIOLOGICAL TREATMENT

1. Use of Existing Organisms For Hazardous Waste Treatment

Process Description --

Microorganisms or their products are actively involved in the degradation of many compounds in the natural environments. These reactions reflect a wide range of metabolic activities and are extremely important in recycling elements useful to living organisms. Many of these reactions can be considered to be adaptations that enable the organisms to interact successfully with their environments. Microorganisms of one kind or another have been able to metabolize a wide range of types of compounds; these abilities have come about through the long process of organic evolution after exposure of the organisms to the presence of the compounds in the environment.

The use of existing organisms for hazardous waste treatment can be by means of conventional applications or by means of innovative applications. Conventional applications of biological treatment include most techniques used for municipal waste treatment, such as, activated sludge, aeration basins, trickling filters, and stabilization ponds. These techniques plus others, such as, rotating biosurfaces, biofiltration, and anaerobic digestion have been reported in the literature to be effective in treating various organic industrial wastes.

Innovative applications of biodegradation techniques include the following: activated carbon adsorption with anaerobic or aerobic regeneration, biological seeding, fluidized bed bioreactor, fixed activated sludge, deep tank

extended aeration, activated carbon addition, pure oxygen systems, deep shaft aeration, limited aeration, cooling tower biooxidation, and automation/ optimization. These applications involve innovative bioreactor design, innovative accessories, or innovative operational methods.

More recently there has been increasing interest and investigation into the use of a specific strain or specific mixed culture of microorganism to detoxicate or destroy organic materials, especially recalcitrant hazardous waste. Most of the studies have involved the testing of populations of single species under controlled laboratory conditions and most of the organisms have been species of bacteria. Examples of some of the microorganisms tested are species of the bacterial genera Pseudomonas, Artrobacter, Bacillus, Clostridium, Escherichia, Hydrogenomonas, Klebsiella, Micrococcus, and Proteus, genera of the Actinomycetes such as Nocardia and Streptomyces, the genera of fungi Aspergillus, Fusarium, Mucor, and Trichoderma, the yeast Saccharomyces, and the algae Chlamydomonas, Chlorella, and Dunaliella. Each of the above is known to metabolize to some extent certain organochloride compounds.

Research funded by the U.S. Environmental Protection Agency indicates that the white rot fungus Phanerochaete chrysosporium is capable of converting the following compounds to CO_2: Lindane, Mirex, benzo(a)pyrene, DDT, DDE, 2,3,7,8-TCDD, 3,4,3'4'-tetrachlorobiphenyl, 2,4,5,2',4',5'- hexachlorobiphenyl, hexachlorobenzene, biphenyl, benzoic acid, p-chlorobenzoic acid, and pentachlorophenol. The data from this research indicate that the degradation mechanism for mineralizing these compounds is the lignin degrading system possessed by this fungus. Continuing research on this organism will determine optimum conditions for the organisms' degradation capability, how well it works under field conditions, purification and characterization of the enzyme or enzymes involved, and determination of the metablic pathway.

Applicability to the Treatment of Hazardous Waste --

The biological treatment methods mentioned above, viz., activated sludge, aeration basins, trickling filters, stabilization ponds, rotating biosurfaces, biofiltration, anaerobic digestion, activated carbon adsorption with anaerobic or aerobic regeneration, biological seeding, fluidized bed bioreactor, fixed activated sludge, deep tank extended aeration, activated carbon addition, pure oxygen systems, deep shaft aeration, limited aeration, cooling tower biooxidation, and automation/optimization stress application in field situations. Much valuable information has been obtained from these studies. These applications involve innovative bioreactor design, innovative accessories, or innovative operational methods. Less emphasis has been placed on identity of the organisms involved. Basic research is going on however to determine which organisms are best for particular pollution problems and to determine the optimum conditions under which the organisms can degrade the pollutants.

Environmental Considerations --

The benefits that can result from the use of biodegradation processes include not only the possibility of reduced operational costs and greater removal efficiencies but also of methods that would not be harmful to the environment. Many of the biodegradation processes take place in nature on naturally occurring chemicals without man's involvement. With man's involvement the potential exists for microorganisms to be able to detoxify recalcitrant compounds polluting the environment without leaving any harmful products of the degradation process.

2. Use of Modified Organisms For Hazardous Waste Treatment

Process Description --

Recent discoveries in biological research have led to an acceleration in man's attempts to alter life forms for his benefit. It is expected that one of

these benefits will be the capability of microorganisms to destroy recalcitrant hazardous wastes. The Hazardous Waste Engineering Research Laboratory supports research projects to develop microorganisms capable of detoxifying hazardous wastes. Emphasis has been on the destruction of halogenated organic compounds in soil polluting situations.

Microorganisms can be modified by techniquies popularly referred to as genetic engineering. By these techniques the genetic makeup of the organism is changed and as a result the organism possesses an improved capability or even one new to the organism. Many microorganisms inherently possess the capability to metabolize the types of compounds that are pollutants in hazardous waste sites or at least can metabolize structurally related compounds. Gene engineering techniques represent a potential means of (1) transferring these capabilities from the types of microorganism in which they are found to the types of microorganism that are best fit to utilize these capabilities in the environment or (2) improving the capability for degradation in specific microorganisms by making them operate faster or more efficiently or (3) increasing the microorganisms' capability to produce the agent responsible for degradation, e.g., an enzyme. Without transferring or changing specific genes by genetic engineering techniques it is also possible to alter life forms through the use of mutagenic agents and through a technique that accelerates the organisms' adaptive capacity. This latter process is known as plasmid assisted molecular breeding (PAMB).

An example of the use of gene engineering to develop a modified organism for use as a degrading agent is a project funded by EPA's Hazardous Waste Engineering Research Laboratory. This effort is attempting to establish in yeast a mammalian gene or genes coding for cytochrome P-450 monooxygenase with the capability of inactivating hazardous waste compounds. This work involves

gene isolation, characterization, sequencing, cloning, and insertion techniques of genetic engineering. Work in this project has progressed to the completion of the gene sequencing stage.

Another project funded by the same Laboratory developed the plasmid assisted molecular breeding technique and through the use of this technique a special bacterial strain was developed. This strain, designated Pseudomonas cepacia AC1100, utilizes 2,4,5-T as a sole carbon source and has been the basis for continuing research to develop a strain capable of degrading dioxins. Biochemical and genetic research using this strain has yielded valuable information on the metabolic pathways and the genes involved in the degradation of 2,4,5-T.

Other projects, supported by a variety of funding sources, are under way to develop modified organisms specifically for the purpose of degrading hazardous wastes. Most of them involve some particular strain of bacterium but other types of organisms are being investigated.

Applicability to the Treatment of Hazardous Waste --

Most of the organismm-modifying research is not oriented to the practical problems of application procedures and most of the projects have not reached the field testing phase. Practical application must first be preceded by survivability tests and tests to determine the impact the modified organism would have upon the environment.

Environmental Considerations --

As with existing organisms the benefits that can result from the use biological degradation processes by modified life forms include the possibility of reduced operational costs and greater removal efficiencies. Any modified organism will not be allowed to be intentionally released if the organism

possesses the capability of doing harm to the environment. The potential exists for these microorganisms to be able to detoxify dangerous polluting chemicals without leaving any harmful products of the degradation process.

SECTION IV

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